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Interaction of Water with Epoxy

Dana A. Powers

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Interaction of Water with Epoxy

D.A. Powers

Advanced Nuclear Energy Programs
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM, 87185-0736
USA

ABSTRACT

The chemistries of reactants, plasticizers, solvents and additives in an epoxy paint are discussed. Polyamide additives may play an important role in the absorption of molecular iodine by epoxy paints. It is recommended that the unsaturation of the polyamide additive in the epoxy cure be determined. Experimental studies of water absorption by epoxy resins are discussed. These studies show that absorption can disrupt hydrogen bonds among segments of the polymers and cause swelling of the polymer. The water absorption increases the diffusion coefficient of water within the polymer. Permanent damage to the polymer can result if water causes hydrolysis of ether linkages. Water desorption studies are recommended to ascertain how water absorption affects epoxy paint.

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NOMENCLATURE

ASTM	ASTM International; formerly American Society for Testing and Materials
BET	Brunauer Emmett Teller method for vapor absorption
BIP	Behavior of Iodine; name of an OECD-NEA
CAS#	number assigned to a chemical species or mixture by Chemical Abstract Service
DGEBA	diglycidal ether of bisphenol A
DIDP	diisodecyl phthalate
EIS	electrochemical impedance spectroscopy
EPICUR	(not an abbreviation) name of a Phébus-IST project
FTIR	Fourier Transform Infrared Spectroscopy
IST	International Source Term [project]
MIBK	methyl isobutyl ketone (4-methyl-2-pentanone)
MSDS	Material Safety Data Sheet
NMR	nuclear magnetic resonance
OECD-NEA	Organization for Economic Cooperation and Development - Nuclear Energy Agency
PALS	positron annihilation lifetime spectroscopy
Phébus	not an acronym - name of a reactor and an in-pile test program

I. INTRODUCTION

The interactions of iodine with painted surfaces have emerged as an important issue in the analysis of reactor accidents sufficiently severe that they release fission products to reactor containments. The Phébus-IST EPICUR and OECD-NEA Behavior of Iodine (BIP) projects have been initiated to study these interactions. Topics of interest include the absorption of molecular iodine (I_2) into paint and the evolution of both molecular iodine and volatile organic iodides (such as CH_3I) when paint is irradiated. The Behavior of Iodine project has produced results that suggest both the absorption of molecular iodine and the subsequent release of gaseous iodine when paint is irradiated depend to some extent on the amount of water the paint has absorbed. It may be that an understanding of water interaction with paint is necessary to predict quantitatively the behaviors of molecular iodine and volatile organic iodides in reactor containments.

The paint that is of immediate interest is epoxy paint. This paint is a complicated mixture based on the polymerization of di-epoxides typically with polyamines. The chemistry of epoxy paint is discussed in more detail in the second chapter of this report. There is not a wealth of information in the publically available literature on water interactions with epoxy paint. Whether this is because of proprietary interest or lack of scientific interest is not known. There is much more information on interaction of water with structural epoxy resins. This scientific interest has arisen because water interactions with epoxy resins can degrade the mechanical properties of the resins [Li *et al.* 2004]. Water can cause the resins to swell and to produce what is called “crazing” of the surfaces. Water absorbed in the resins can reduce the glass transition temperature (T_g) of the polymers and make them weaker.

Epoxy resins are, of course, not identical to the epoxy polymers found in paint. Resins are more rigid and lack the flexibility that is crucial to the functioning of paints. Resins lack the admixtures for color and adhesion characteristic of paints. But, on a molecular level, there are similarities. Certainly, the polar centers in the polymer that are left after reaction of the functional groups of the polymeric reagents should be similar. Physical interactions of water with polymeric surfaces might well have similarities. Consequently, an examination of the literature concerning water interactions with epoxy resins was undertaken. The effort was to gain at least a qualitative if not a quantitative understanding of the ways water interacts with epoxy polymers.

Analytic methods of remarkable sophistication have been applied to understand how water interacts with epoxy resins. An example that will be discussed in more detail in the third chapter of this report is positron annihilation. It is not evident that either the EPICUR or BIP projects are in a position to apply such sophisticated methods to the understanding of water interactions with epoxy paint. On the other hand, some classic, simpler methods have yielded useful insights into water interactions with epoxy resins. A second objective of this examination of the literature of water interactions with epoxy resins has been to identify experimental methods that can be usefully applied to water interactions with epoxy paints.

II. COMPOSITION OF AN EPOXY PAINT

Paints are very complicated mixtures. Epoxy paints are especially complicated because the paint involves two components sometimes called the “resin” and the “cure”. These components react chemically during placement on surfaces. Epoxy paints are suited especially for the coating of metal surfaces to prevent corrosion. Formulation of the resin and the cure owes more to empiricism than to scientific analysis. Ingredients are included to ensure flexibility, chemical inertness and adhesion. Corrosion protection is so economically necessary there is a strong proprietary interest in the formulations of individual varieties of paint. Consequently, paint formulations are not published expansively. In addition, there is a great variety of formulations both within product lines of individual manufactures and among the many manufacturers of paint. Even paints intended for identical applications can have distinct formulations.

A comprehensive examination of paint formulations is not attempted here. Instead, a single paint is examined with the intention of focusing the examination of water interactions on epoxy resins that have similarity to epoxy polymers in paints. The single paint is examined in the detail that is possible given the constraints of trade secrets. The paint that is examined is Amerlock 400. This paint is selected because it is the paint being studied in BIP and has similarities to the Ripolin paints being studied in the EPICUR project.

The compositions of the resin and cure have been derived from Material Safety Data Sheets (MSDS). The compositions so obtained are shown in Table 1. Material Safety Data sheets provide compositions of complex mixtures at some point in time. Compositions of industrial mixtures like paint evolve in response to competitive pressures, customer needs and the availability of ingredients. It cannot be assured that the exact paint composition examined here is currently available.

Though the MSDS list ingredients, they do not describe the purposes of the ingredients. Some of the constituents could serve multiple purposes. Consequently, the purposes ascribed to ingredients in Table 1 are admittedly speculative and subject to revision.

The composition of the resin and cure for Amerlock 400, overall, consist of:

- mineral whiteners
- solvents
- polymer reagents

Table 1. Constituents of Amerlock 400 Paint Inferred from MSDS.

Amerlock 2 / 400 Resin			Amerlock 400 Cure		
species (CAS#)	wt. %	comment	species	wt. %	comment
DGEBA (25085-99-8)	50	epoxy resin	xylenes (1330-20-7)	12.5	solvent
titanium dioxide (13463-67-7)	30	whitening	ethyl benzene (100-41-4)	3	solvent
magnesium silicate (14807-96-6)	15	whitening	nonyl phenol (84852-15-3)	10	plasticizer and chain terminating reactant
diisodecyl phthalate (68515-49-1 or 26761-40-0)	5	plasticizer	polyoxypropylene diamine (9046-10-0)	10	reactant
high flash naphtha (64742-95-6)	2.8	solvent	diisodecyl phthalate (68515-49-1 or 26761-40-0)	5	plasticizer
1, 2, 4-trimethyl benzene (95-63-6)	2.1	solvent	furfuryl alcohol (98-00-0)	5	chain terminating reactant
			polyamide resin* (68410-23-1)	15	see footnote
			barium sulfate (13462-86-7)	25	whitening
			magnesium silicate (14807-96-6)	25	whitening
			clay (68911-87-5)	5	whitening
			amine carboxylate	5	preservative

*polyamide resin is the common name for the reaction products of mixed dimeric C-18 fatty acids (oleic acid, linoleic acid and linolenic acid) with polyethylene polyamines.

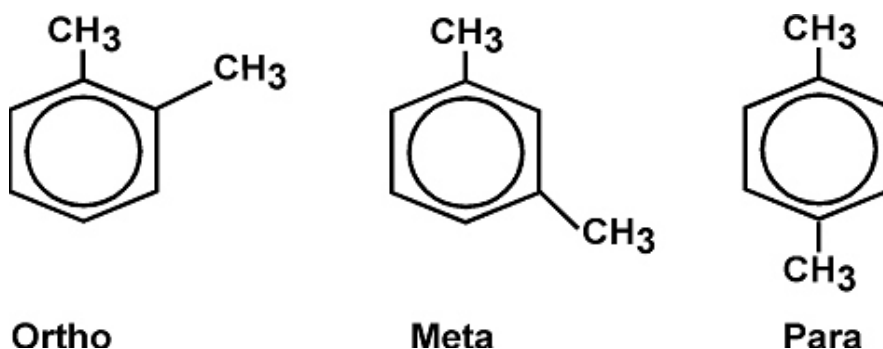
- plasticizers
- other additives for adhesion, preservation and stability

The mineral constituents (barium sulphate, titanium dioxide, etc.) are present for cosmetic purposes primarily, though they may protect paints from ultraviolet radiation damage as well. They are not further discussed here.

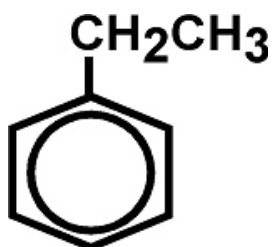
The organic constituents of the paint are discussed in the subsections that follow.

A. Solvents

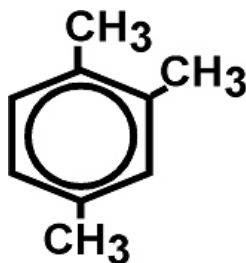
Solvents listed in Table 1 include a mixture of xylenes:



ethyl benzene:


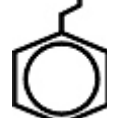
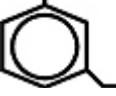

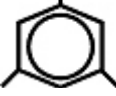
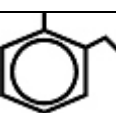
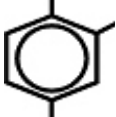
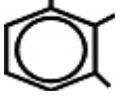

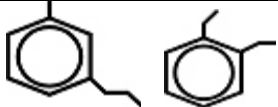
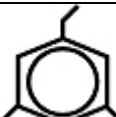


and 1,2,4- trimethyl benzene (sometimes called pseudocumen):



The formulation for the Amerlock 400 resin includes “high flash aromatic naphtha” which is a light aromatic hydrocarbon solvent. Common marketed versions of high

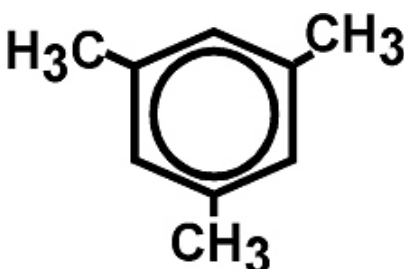
Table 2. Chemical composition of high flash aromatic naphtha. Values are given in weight percent.

Species	Clark <i>et al.</i>	Schreiner <i>et al.</i>	
o-xylene	2.27 w/o	3.20 w/o	
n-propylbenzene	4.05	3.97	
1-methyl-3-ethylbenzene	7.14	15.1	
1-methyl-4-ethylbenzene	16.6	7.05	
1,3,5-trimethylbenzene (mesitylene)	9.35	8.37	
1-methyl-2-ethylbenzene	7.22	5.44	
1,2,4-trimethylbenzene (pseudocumen)	32.7	40.5	
1,2,3-trimethylbenzene	2.76	6.18	
isopropylbenzene	1.77	NR	
1-methyl-3-n-propylbenzene + 1,2-diethylbenzene	6.54	not reported	
1-ethyl-3,5-dimethylbenzene	1.77	not reported	
nonaromatic	0.46	not reported	

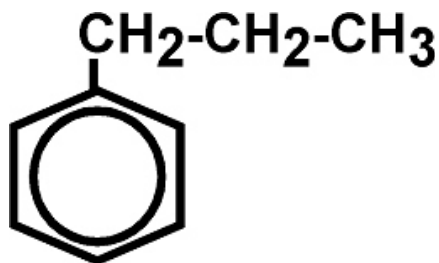
flash aromatic naphtha include Aromatic 100, Solvesso 100 and ShellSol A. These are products of distillation, so the chemical composition undoubtedly varies from supplier to supplier and within batches provided by a particular supplier. Compositional specification have not been found for any of the commercial products. There have been toxicological studies of high flash aromatic naphtha that report compositions. Clark et al. [1989] examined the inhalation toxicology of a mixture composed of equal parts ShellSol A and Solvesso 100. The chemical composition reported by these investigators is shown in Table 2. Schreiner *et al.* [1989] studied the mutagenic potential of a generic high flash naphtha that conformed to the specification in ASTM method D-3734. The chemical composition they reported is also shown in Table 2. These results show that high flash aromatic naphtha is predominantly 1,2,4-trimethylbenzene (sometimes called pseudocumen), 1,3,5-trimethylbenzene, and 1-methyl-3-ethylbenzene.

Ball *et al.* [2003] have examined the water leaching of these solvents from paint. Verdin [1963] has examined the radiolysis of xylene isomers and ethyl benzene with and without molecular iodine present. He finds the predominant products of radiolysis are hydrogen ($G \sim 0.2$ molecules/ 100eV absorbed dose), methane ($G \sim 0.014$) and a polymeric hydrocarbon ($G \sim 1.0$) having a molecular weight of about 270. Molecular iodine suppressed the production of methane during radiolysis. No mention was made of the formation of organic iodides during the irradiation of these solvents in the presence of molecular iodine.

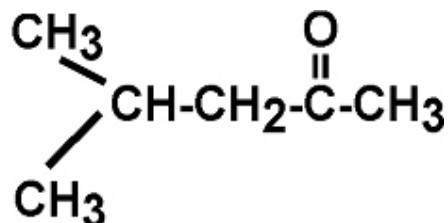
Some formulations for the cure use alternative but functionally equivalent solvents such as mesitylene (1,3,5-trimethyl benzene):



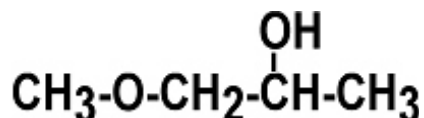
and propylbenzene:



Interestingly, there is no mention of methyl isobutyl ketone (4-methyl-2-pentanone also MIBK):



which is often cited as an important solvent in paint [Wren *et al.*, 2000]. This does not mean that methyl isobutyl ketone was never used in Amerlock 400, nor does it mean that methyl isobutyl ketone is not used in other paints found in reactor containments. Indeed, Amercoat 66, another epoxy paint, does contain methyl isobutyl ketone in the cure. There is, however, no mention of methyl isobutyl ketone in the MSDS examined for either the resin or the cure of Amerlock 400. Methyl isobutyl ketone may be incorporated into the paint during application on surfaces. Some, similar, epoxy resin formulations mention propylene glycol monomethyl ether (1-methoxy 2-propanol) as an ingredient:

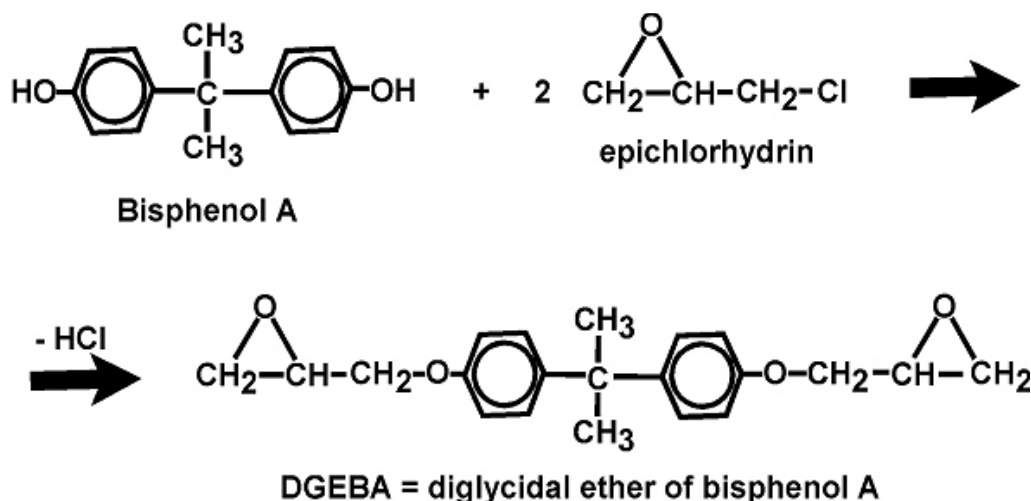


This liquid is usually considered a solvent for cellulose.

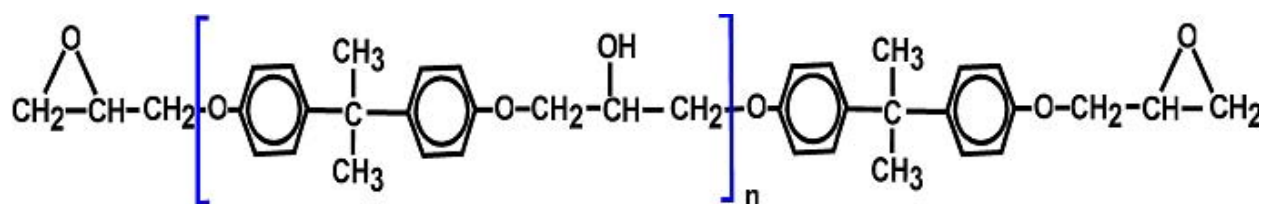
B. Polymer Reagents

1. Resin

The reagent from which epoxy paint gets its name is the diglycidal ether of bisphenol A (4,4' dihydroxy-2,2-diphenyl propane). The ether is formulated by the treatment of bisphenol A with epichlorhydrin (1-chloro-2,3-epoxy propane or chloromethyl oxirane):



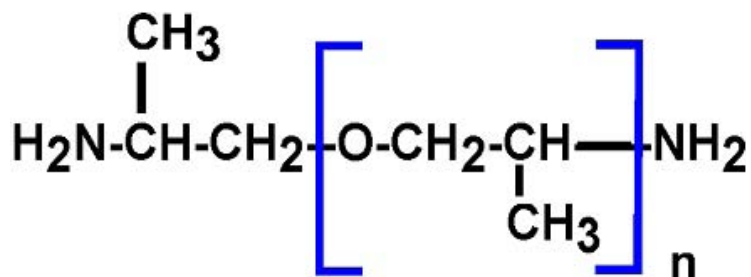
This di-epoxy reactant is often designated DGEBA. The chain of bisphenol groups can be extended and the product is still called DGEBA:



Polymer reactants with n between 0 and 25 are used for a variety of applications. There is some indication in the MSDS that the molecular weight of the reagent is less than 700 which implies that the value of n in Amerlock is about 1. The longer chain should yield a more flexible polymer, but there will be some tendency for crystallization which is undesirable in paint.

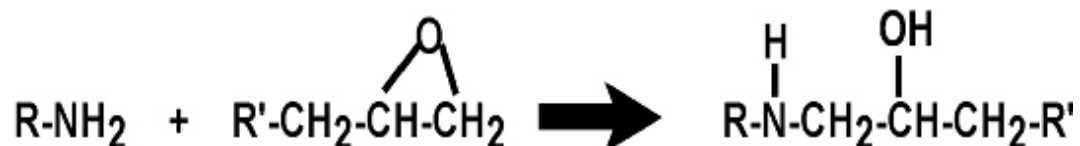
2. The hardener

To form an epoxy polymer, the usual reaction is with an amine though non-amine reactants can be used. The amine reactant is sometimes called "the hardener". Its mixture with other ingredients is called "the cure". In the case of the Amerlock 400 cure, the hardener is polyoxypropylenediamine:



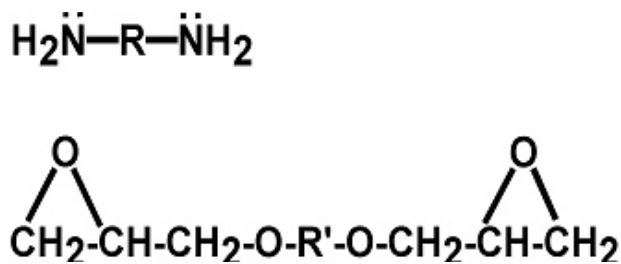
where n may be between 5 and 6.

The general epoxy-amine reaction is:



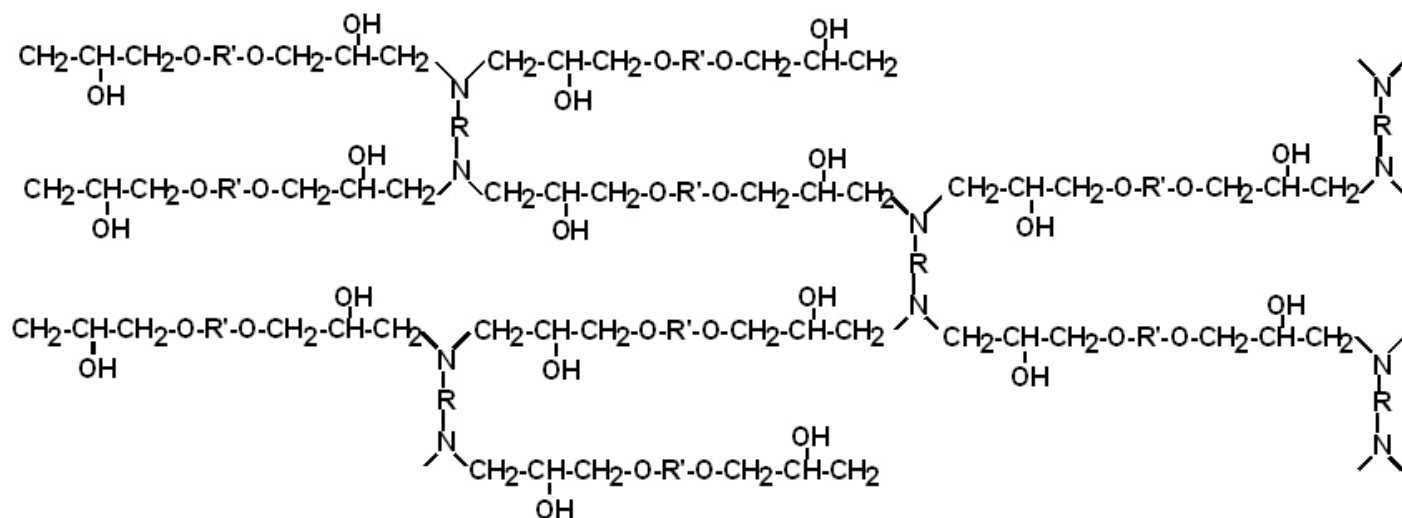
The secondary hydroxyl group left after reaction can react, in principle, with another epoxy group. Very often there are steric constraints that prevent this reaction. Residual secondary hydroxyl groups are thought to be responsible for the strong adhesion of epoxy polymers to metal surfaces. As discussed further in Chapter III of this report, some feel that this secondary hydroxy group plays an important role in the absorption of water by epoxy resins. Marchand [1997] has suggested that under acidic conditions the carbon attached to the hydroxide group may be susceptible to nucleophilic substitution by iodide ion.

To economize on the nomenclature in discussion of the polymerizations, the reactants are abbreviated here as:



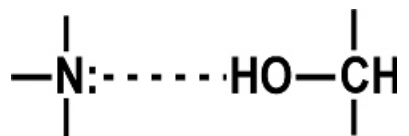
where R and R' designate the lengthy organic chains separating the functional groups.

These abbreviations emphasize the multifunctional natures of the reactants. DGEBA is difunctional. Because both hydrogens on each amine of the polyamine are reactive, the hardener is tetra-functional. With these multifunctional reagents, a very complicated polymer network can form:



In principle, a single macromolecule could be formed. In the viscous medium of paint, however, there are constraints on the mass transport and mixing of reactants that will limit the extent of reaction. As a result, the polymeric network is never complete. Unreacted secondary and even primary amines will be trapped within the polymer network. Aujollet [1999] has called attention to the possibility that molecular iodine may associate with amines as part of a charge transfer complex. The product epoxy resin consists of many three dimensional networks of variable molecular weight. The average molecular weight of the polymer segments has a bearing on the properties of the polymers. The molecular weight can be tailored by including in the reactive mixture mono-functional species that will terminate locally the chain of reactions that create the polymer.

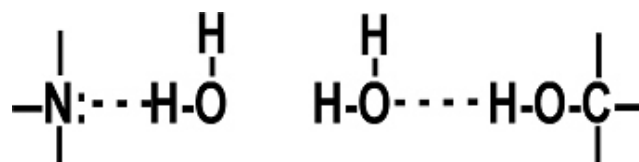
The functional centers of the network formed by the polymerization reaction are the tertiary amines and the secondary hydroxyl groups. The tertiary amines can be protonated to form ammonium groups and the proton on the secondary alcohol is mildly acidic. It is, then, probable that hydrogen bonds form among segments of the polymeric network:



Hydrogen bonding between the hydroxyl and the tertiary amine should be the strongest

in the epoxy resin, but other hydrogen bonding can occur. There can be hydrogen bonding between the ether oxygen and the hydroxyl group or even between two hydroxyl groups [Soles and Lee, 2000]. Hydrogen bonding among segments will densify and strengthen the network.

The hydrogen bonds among polymer segments are, however, disrupted by any water that is absorbed into the polymer network. Water is more acidic than the secondary hydroxyl group and has higher electron density than the functional centers of the network:

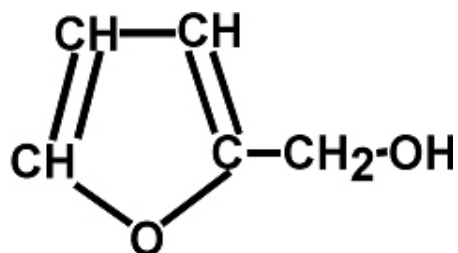


This disruption of hydrogen bonds can swell and plasticize the polymer (See Chapter III).

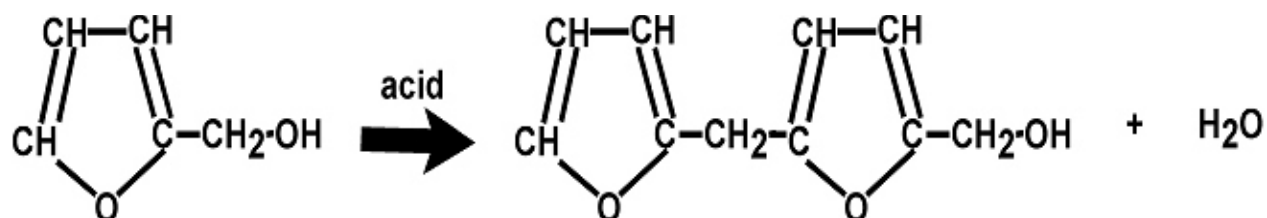
3. Chain termination

It is possible that polymerization in diverse circumstances of paint applications will yield excessive crosslinking either globally throughout the polymer or locally at peculiar points having unusual mass transport characteristics. This could make the resin so rigid that it lacks the flexibility expected of paint coatings. To prevent this, monofunctional constituents are included in the Amerlock 400 cure. These monofunctional reactants will terminate network formation by reaction with the di-epoxy reagent, DGEBA. The ingredients taken to be present to terminate reaction and limit the extent of crosslinking are furfuryl alcohol and nonyl phenol.

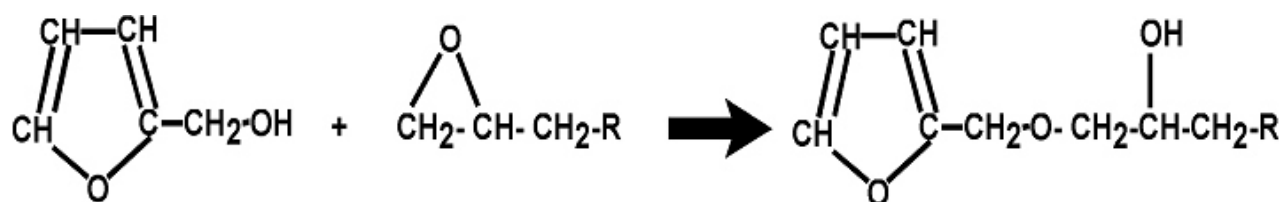
Furfural alcohol is:



Furfural alcohol will self polymerize under acid conditions:

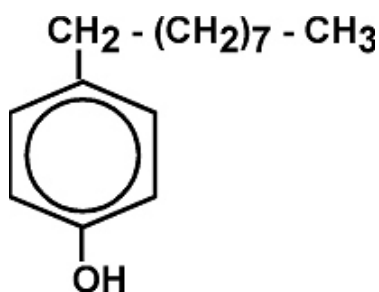


This polymer of furfural alcohol is used for sand casting and might be present to stabilize the mineral constituents of the paint. But, the amines in the formulation make paint a basic medium that should not promote self polymerization. It appears more likely that the function of furfural alcohol is to serve as a chain terminator to avoid excessive cross linking of DGEBA that might make the polymer too rigid or crystalline:



Because there is only a single, reactive functional group in furfural alcohol, polymerization is arrested at the site where it reacts if epoxides cannot gain access to the product secondary hydroxyl group.

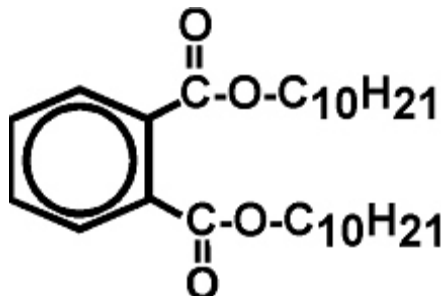
Another additive that can terminate polymerization by reacting with epoxide groups is nonyl phenol:



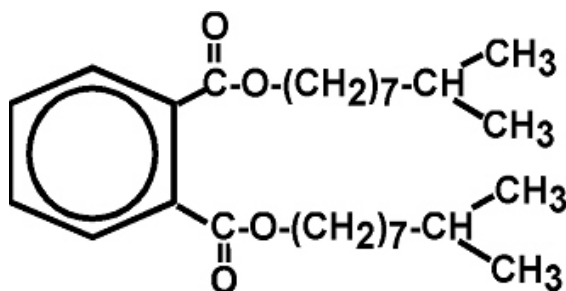
The phenolic hydroxyl group will react with the epoxide groups on DGEBA much like the hydroxyl group of furfural alcohol. Again, because nonyl phenol has but one functional group, reaction with an epoxide group can terminate the polymerization locally.

C. Plasticizers

Plasticizers are included in paint formulations to prevent crystallization of the polymer segments. Diisodecyl phthalate is a well known plasticizer included in both the resin and the cure of Amerlock 400:



This plasticizer, sometimes designated DIDP, is most likely a complicated mixture of isomers. Interestingly, it is assigned two CAS numbers (See Table 1). The most common isomer is thought to be:



Isomeric content, of course, inhibits crystallization of the cured polymer. It also widens the liquid range of the constituents to promote mass transport during the polymerization process. Presumably, this ester can be hydrolyzed under the right conditions by water that is absorbed into the paint.

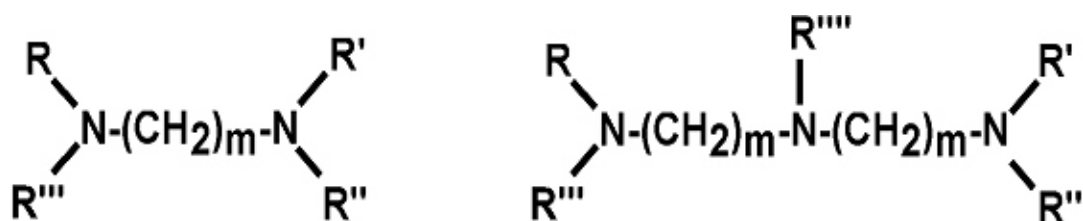
D. Additives

Additives are other ingredients included to either tailor the properties of the polymer or to stabilize the components prior to use. Two additives are present in the cure for Amerlock 400 and are discussed in the sections that follow.

1. Amine carboxylates

An additive to the Amerlock 400 cure is a mixture designated “amine carboxylate”. This mixture is not further identified in information that has been found to date. Amine carboxylate usually designates a mixture of carboxylate salts of tertiary amines. A common formulation of amine carboxylate used industrially involves tertiary diamines

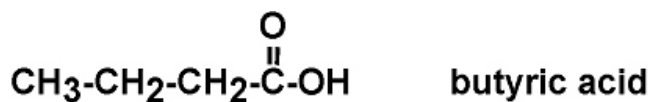
and triamines (m = 1 to 6):



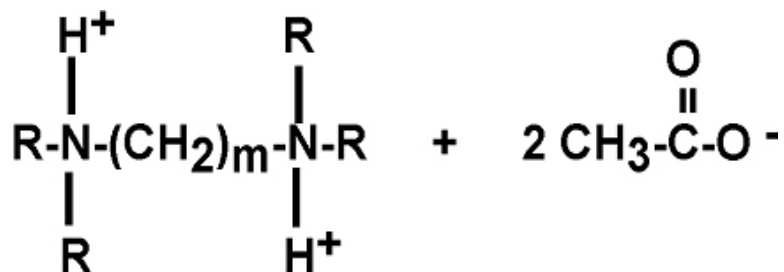
The substituents on the tertiary amines, R, R', R'', R''', and R''', are randomly selected from:



Associated with these amines are the low molecular weight carboxylic acids:

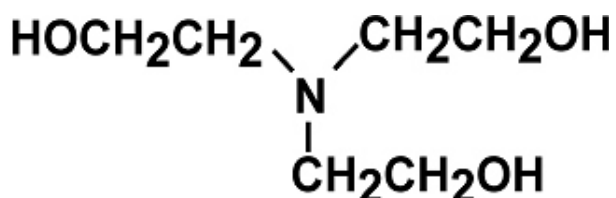


The acids will protonate the tertiary amines to create the carboxylate salts. For example, with acetic acid and a diamine:



Of course, there is no assurance that the typical formulation of amine carboxylate depicted here is the material included in the Amercoat 400 cure.

It is not readily apparent why the salt mixture is included in the formulation of the cure. It may limit the ability of ions to penetrate the paint coating and participate in corrosion of the underlying substrate. The tertiary amine, triethanol amine (or in the nomenclature above, m=1, p=2), is used to prevent particle agglomeration in such diverse applications as cement clinker and makeup [Sohoni, *et al.*, 1991]:

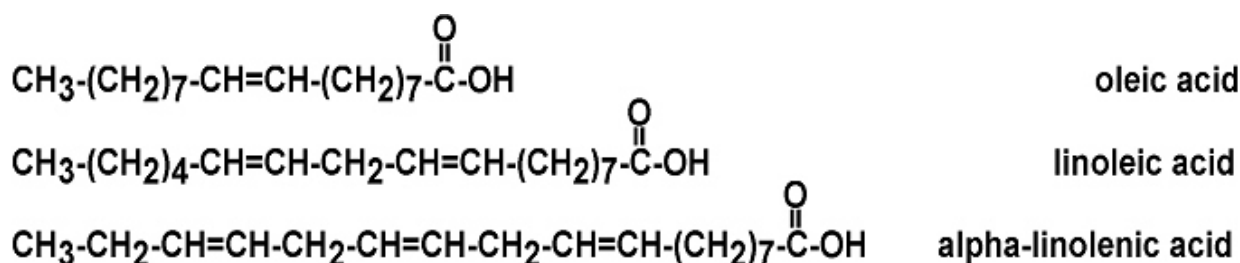


It is likely that the protonated tertiary amines formed by the amine carboxylates performs the same function for the inorganic particles (whiteners) in the paint.

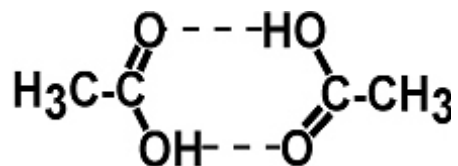
Absorption of water into the paint could protonate the carboxylate anions of the amine carboxylate. Protonation of the short chain carboxylates in the hypothetical formulation shown here would yield carboxylic acids with very high water solubility.

2. Polyamide resin

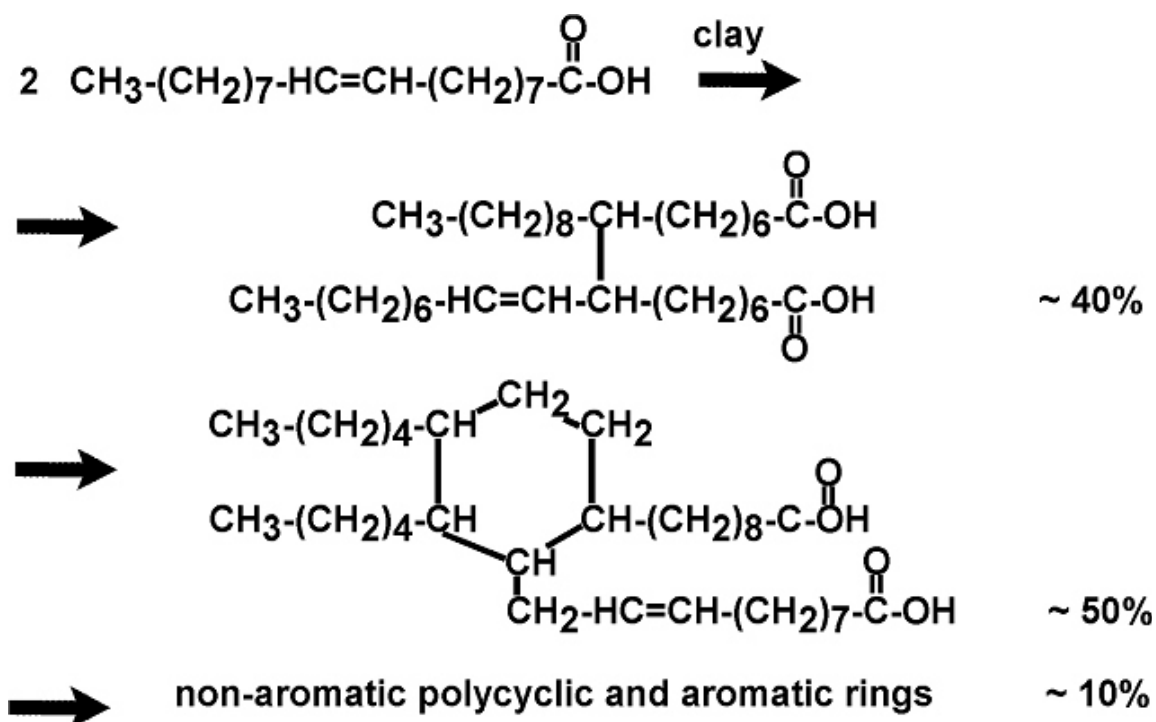
“Polyamide resin” is another additive to the cure. This additive is a type of nylon. Based on the chemical abstract number (CAS#) this material is the product of reaction between C-18 unsaturated fatty acid dimers with polyethylene amines. The unsaturated C-18 fatty acids are, of course, the well known oleic, linoleic and -linolenic acids:



Dimerization of these unsaturated acids does not refer to the hydrogen bonding familiar in the discussion of low molecular weight carboxylic acids:

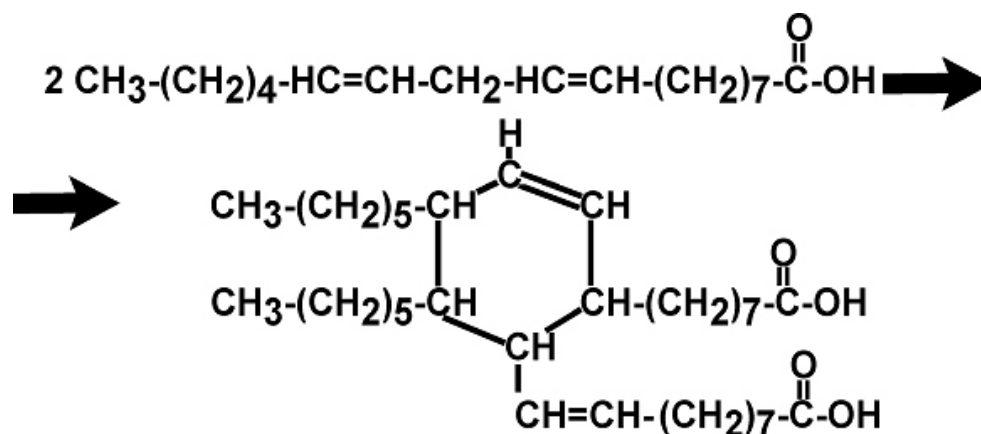


Dimerization converts the monofunctional, long-chain acids into dicarboxylic acids that will sustain polymerization. The reaction is usually done at elevated temperatures and pressures over a clay catalyst with some small amount of water present. McMahon and Crowell [1974] have discussed the publically available information on the products of dimerization of oleic acid. They suggest:

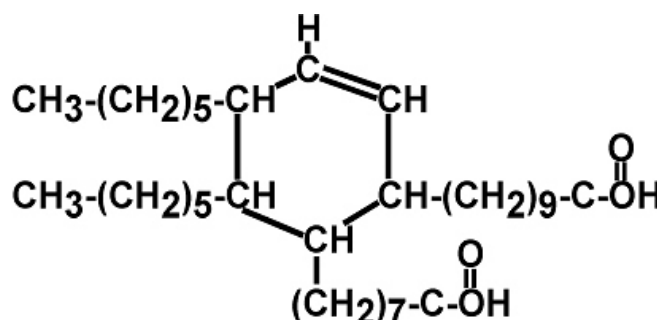


Trimerization also occurs in the catalytic process. The trimeric products can be quite complicated.

Dimerization of linoleic acid may be somewhat simpler than the dimerization of oleic acid. Natural linoleic acid does not have conjugated double bonds. Heat treatment during the dimerization will conjugate the double bonds of natural products much like the double bonds in synthetic linoleic acid. The conjugated double bonds make linoleic acid more likely to form non-aromatic rings during dimerization by a Diels-Alder reaction [Wheeler *et al.* 1971]:



Dimerization of a mixture of fatty acids is, however, more likely to yield a mixed product of reaction between oleic acid and linoleic acid:



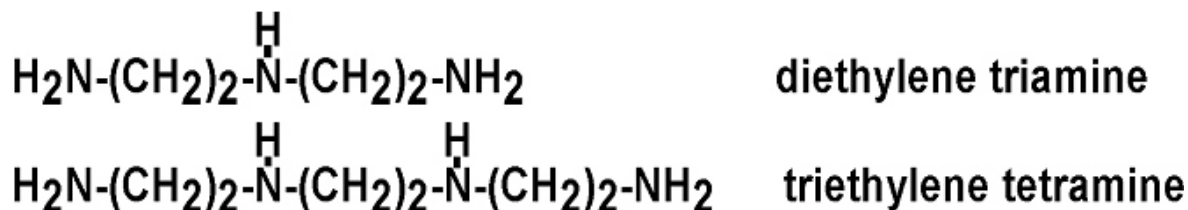
Dimerization of linolenic acid does not appear to have been studied extensively. Again, when fatty acid mixtures are subjected to treatment by the dimerization process, it is likely that the more abundant oleic acid reacts linoleic acid, again by a Diels-Alder mechanism, to form monocyclic and polycyclic products.

Typically, the dimerization of fatty acids is incomplete. It is not uncommon for 20 to 30% of the monomeric acids to remain undimerized. The dimerization process is sufficiently harsh that there is some methyl migration in the monomers to yield isomeric products. There can be some hydrogen exchange so that saturated acids are formed. The isomeric mixture may have some advantages since it will prevent crystallization and will broaden the liquid range for polymerization reactions. Monomers will, of course, keep molecular weights of polymers low by terminating the chain of reactions.

The product of dimerization can be enriched in dicarboxylic acids (up to 97%) by distillation. It is not known whether the polyamide resins used in epoxy paint have been formed using the raw or distilled products of the dimerization process. Polyamide resins formed by reactions with fatty acids are used in inks to enhance adhesion to slick, plastic surfaces. Some formulations of the polyamides for use in inks call for inclusion of 10-15% of monomer fatty acid in the reactive mixture.

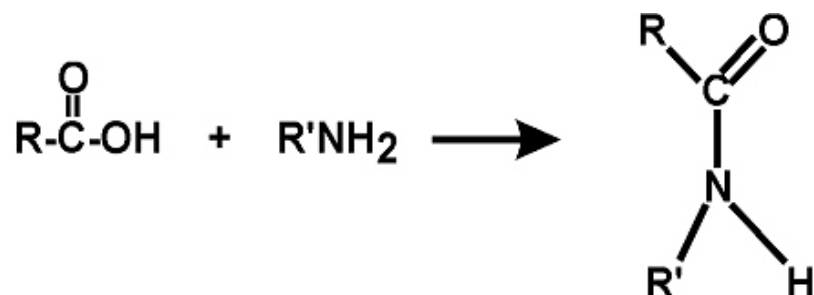
Dimerization preserves some of the double bonds present in the fatty acids. These double bonds can be hydrogenated readily under mild conditions with noble metal catalysts. It appears that this is done sometimes. Whether it was done to the reactants used to form the polyamides for use in the epoxy cure of paint is not known.

To form the polyamide additive, the fatty acid dimer mixture is reacted with polyethylene polyamines such as:



Formulations also include tetraethylene pentamine and even pentaethylene hexamine. The precise composition of the amine mixture used to form the polyamide additive to the Amerlock 400 cure is not known.

The obvious reaction of the amines with the fatty acid carboxylic functional group yields an amide:



Of course, because the amines are polyfunctional, what is formed is a polymeric network of amide linkages. The diversity of both carboxylic acid and polyamine reactants assures that there is little of the crystallinity in the polyamide of the type familiar in nylon fibers.

Fatty acids are well known to absorb on iron oxide [Wheeler *et al.*, 1971]. It is likely that even when reacted with the amines, the long chains of these fatty acids still absorb on oxides. This property may be exploited in paint to enhance adhesion to metallic surfaces with oxide surface layers.

The presence of polymeric amide additives in the paint cure is most significant in terms of iodine interaction with paint since it is well known that polyamides (nylon) readily absorb iodine [Murthy, 1987]. Singhal and Ray [2002] found that the amount of iodine

absorbed by nylon from an acetone solution in 48 hours at 298 K correlated with the iodine concentration according to:

$$m = 60400 C^{1.5625}$$

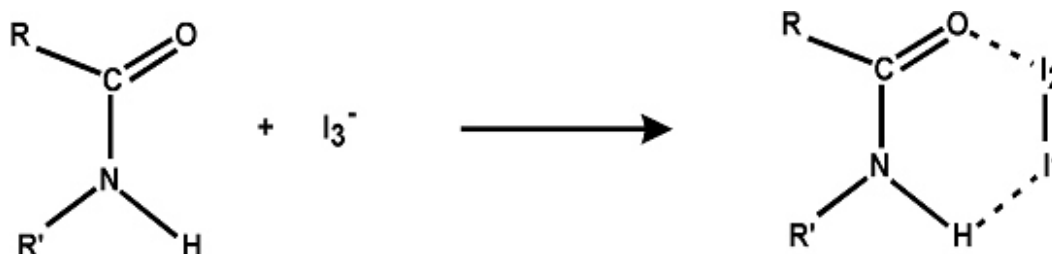
where:

m = mass of iodine absorbed (μg per g polymer)

C = molar concentration of I_2 in solution

They also found that nylon absorbed molecular iodine from the gas phase. The absorption varied with the partial pressure to the power 0.59. This contrasts with the linear dependence found by Aleksandrov *et al.* [1996] for the absorption of iodine by epoxy paints. Sukawa *et al.* [1987] found that nylon would absorb about 1.7 grams of molecular iodine per gram of nylon from a 0.1 M aqueous solution.

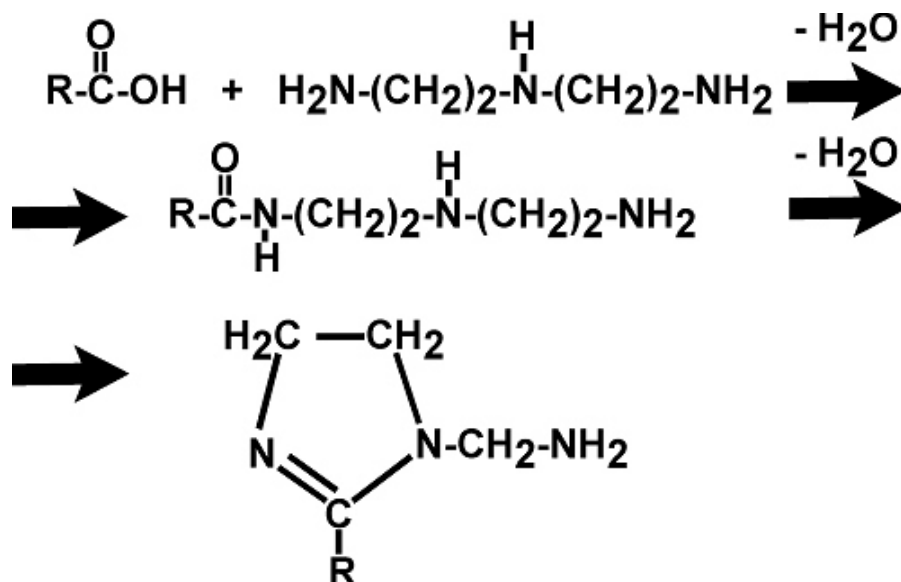
Maillo *et al.* [2005] used FTIR to examine the changes in the nylon structure caused by the absorption of iodine from aqueous solution at concentrations of 0.03 to 2 M. They interpreted their spectra to indicate that the absorbed species is I_3^- and that it is bound to the amide group:



Water, they argued, facilitated the absorption of iodine by disrupting hydrogen bonds within the polymer to provide access to amide groups.

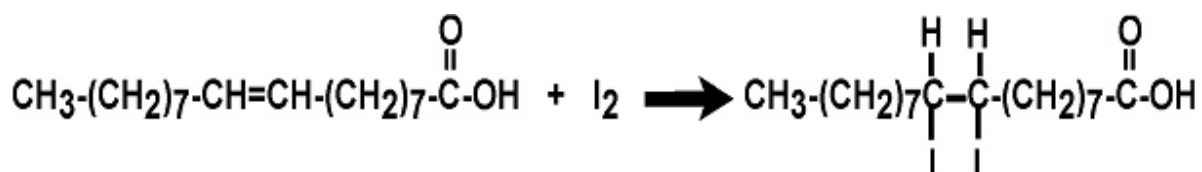
Murthy [1987] used X-ray techniques to deduce that both I_3^- and I_5^- were present in fibrous nylon exposed to aqueous iodine solutions. Their analysis showed the absorbed iodine species to be quite similar to the iodine species absorbed from aqueous solution by amylose [Xu *et al.*, 1996]. The orderly array of polyiodide anions found in the x-ray studies of relatively crystalline nylon may not develop when the amorphous polyamide additive used in the Amerlock 400 cure is exposed to iodine solutions.

When diethylene triamine is present, there is an alternative reaction that leads to the formation of imidazoline:



Oleic imidazoline is known to be an inhibitor of corrosion because it absorbs on the oxide surface film of carbon steel [Ramachandran and Jorancicevic, 1999] [Ramachandran *et al.*, 1997] [Edwards *et al.*, 1994]. Formation of this product, if it occurs, would contribute to the corrosion protection provided by epoxy paint.

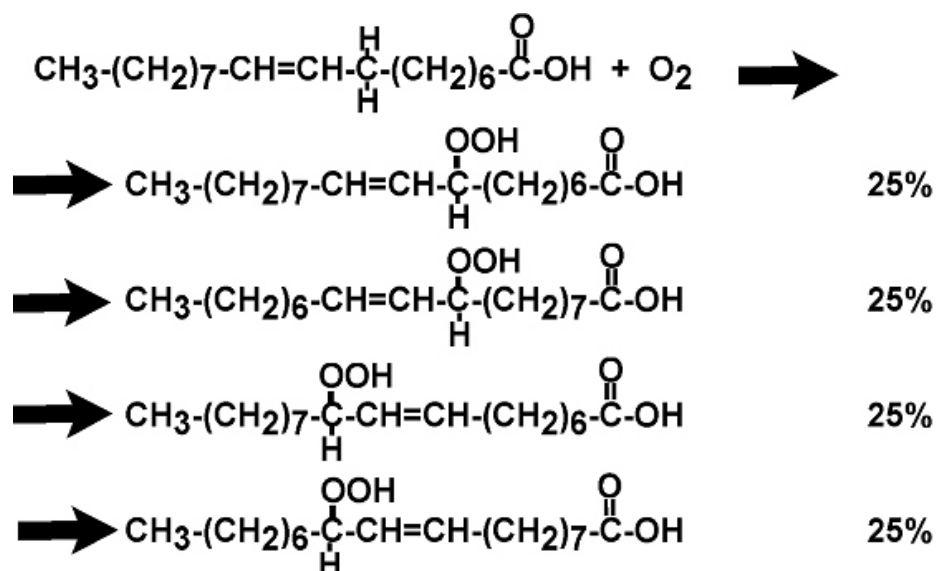
It is not certain that the unsaturation of the fatty acids is preserved in the polyamide resin added to the Amerlock paint. If any significant amount of unsaturation remains it is significant with respect to iodine interactions with the paint. A fairly common method to determine the unsaturation of fatty acid mixture of the type used in formulating the polyamide discussed here is the "iodine number" [ASTM, 2006]. Under rather mild conditions iodine will add across the double bond for example in oleic acid:



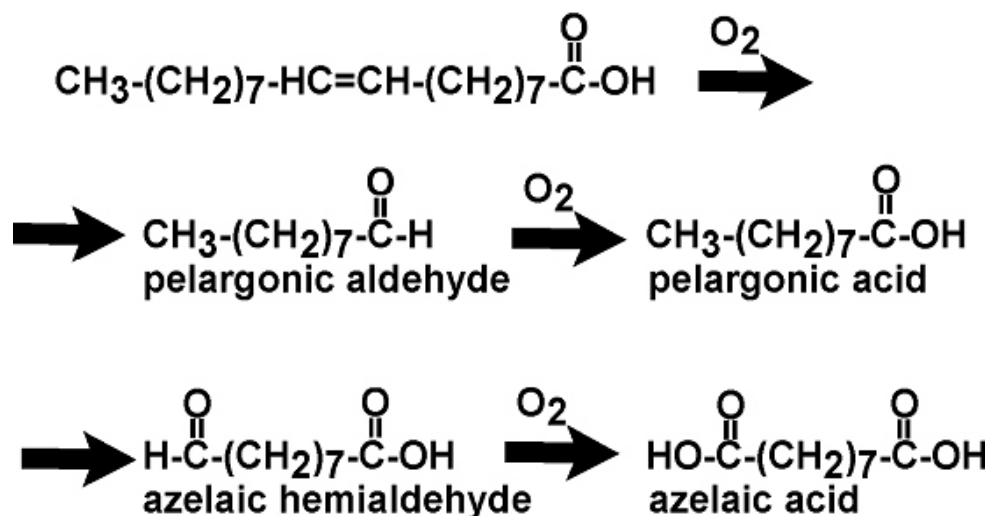
Similar reactivity of unsaturated fatty acid chains on polyamides would be expected in view of the distance between the double bonds and the amide linkages.

Under mild conditions, the iodine adduct across a carbon-carbon double bond can decompose and the iodine is released. This susceptibility of the iodide is of interest with regard to the evolution of iodine from paints exposed to radiation.

The unsaturated fatty acid chains are also susceptible to oxidation - it is what makes fatty acids become rancid. The allylic hydrogen on the carbon adjacent to the double bond is particularly labile, so when oleic acid (9-octadecenoic acid) is exposed to oxygen several products form:



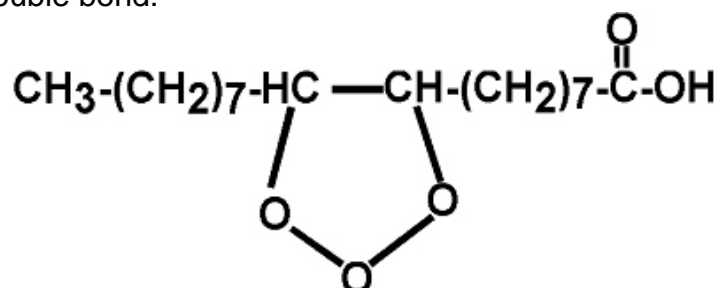
The carbon double bond is weakened. Ideally, the hydroperoxides dissociate into pelargonic aldehyde (n-nonanoic acid) and azelaic hemialdehyde. With continued oxidation these products are converted into pelargonic acid (n-nonanoic acid) and azelaic acid (1,9 nonadioic acid):



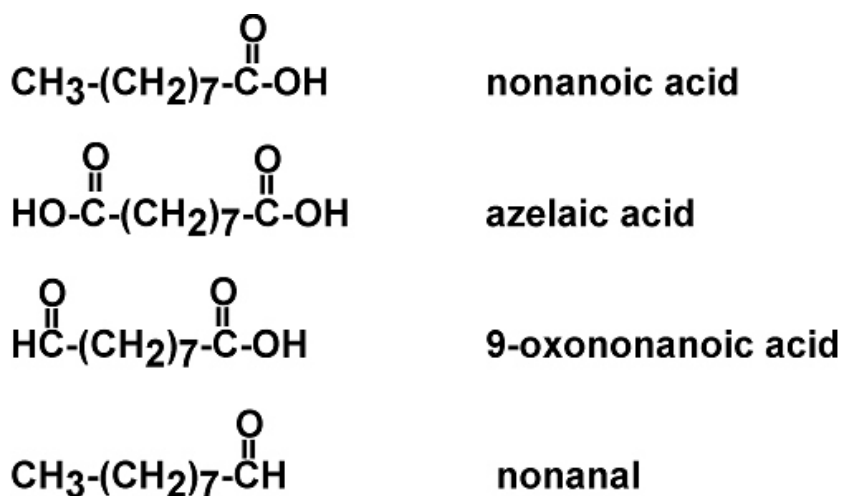
These acids are industrially important since they have odd numbers of carbon atoms which is unusual in nature. These acids with odd numbers of carbon atoms exhibit unusually strong adsorption on metal surfaces and can inhibit corrosion.

The oxidation of oleic acid is sensitive to the strength of the oxidation. The decomposition of the hydroperoxide may not occur ideally. A patent assigned to Synergistic Industries, Inc. [U.S. Patent 5380928] describes oxidation of oleic acid with concentrated nitric acid at 293-298 K that yields 44-45% azaleic acid, 16-17% siberoc acid (pctamedioic acid), 712% pimelic acid (heptanedioic acid), 6-10% succinic acid (butanedioic acid and pentanedioic acid), 3-4% adipic acid (hexanedioic acid) and 0-2%sebacic acid (decandedioic acid). It is, then, difficult to predict products of air oxidation of fatty acid chains in epoxy paints.

In a radiation environment reaction of oleic acid with ozone is of interest. Ozone adds across the double bond:



This intermediate product decomposes to produce a variety of species including [Ziemann 2005]:



Nonanal is noteworthy for its volatility.

More complex products can form [Zahardis *et al.* 2006] especially if additional oleic acid is readily available [Katrib *et al.*, 2004]. For a review see [Zharardis and Petrucci, 2007].

The susceptibility of unsaturated fatty acid chains to oxidation even when reacted with amines may be a property desirable for paint formulations. In service,

preferential reaction with the polyamide would protect the more essential features of the paint from oxidation and ultraviolet radiation.

III. EXPERIMENTAL INVESTIGATIONS OF WATER INTERACTIONS WITH EPOXY RESINS

Epoxy resin is a principal ingredient of epoxy paint. Water absorption is endemic to epoxy resins. The absorption is associated with the tertiary amine and hydroxyl groups formed in the polymerization process [Van Krevelen and Hoftyzer, 1976]. As noted in the introduction, water absorption by epoxy resins has been extensively studied because of its impact on the structure properties of these resins. Here, studies of water interactions with epoxy resins are examined to gain some qualitative insights into the ways water might interact with epoxy paint. Of course, the many other constituents of paint discussed in the previous chapter could affect water interactions. The examination of water interactions with epoxy resin, then, provides a first, simple, starting point that may subsequently be refined. The examination of studies of epoxy resins also provides information on the kinds of experimental techniques that have been applied to the understanding of water interactions with polymers and how results obtained by various methods can be interpreted.

Structural epoxy resins have more crosslinking and are even prepared at elevated temperatures to assure more complete reaction of the polymerization reagents. This treatment could affect the interactions of the resin with water. Abdelkader and White [2005] explicitly examined the effects of heat treatment on the water interactions with resin. For these studies, they used DGEBA polymerized with diethylenetriamine among other polyamines. Exposure to water was by immersion. The water absorption by a resin prepared and maintained for four weeks at 296K is compared in Figure 1 to water absorption by a resin prepared by heating to 423 K for four hours. The heat treated specimen absorbed about the same amount of water as the specimen prepared by gentler methods and aged for 4 weeks. The water diffusion coefficient derived from the two sets of absorption measurements was about the same $-1.3 \times 10^{-9} \text{ cm}^2/\text{s}$. The similarity of water absorption by the DGEBA-diethylenetriamine resins was not a general result and other polymer systems exhibited quite different water absorption properties depending on the temperature of reaction.

The early literature of water interactions with epoxy resin deals with the ways water can interact with the polymer. Apicella *et al.* [1984] identified three modes of interaction:

- adsorption on hydrophilic centers on surfaces defining the void structure of the resin
- condensation within the void structure
- absorption and presumably bonding with the polymer network.

These investigators used pressurized water (up to 60 bars) to saturate an epoxy resin. They found that water absorption permanently altered the structure of the polymer network. Furthermore, they found that cooling a resin to 293 K after saturating the resin at 333 K led to further water absorption.

Moy and Karasz [1980] conducted BET studies of epoxy polymers using water vapor at temperatures from 298 to 318 K. They found that Type II isotherms were developed (see Figure 2). Such isotherms are indicative of very strong interactions of a first monolayer of water with the surface relative to interactions of subsequent monolayers with underlying water molecules. This is consistent with the hypothesis that water molecules hydrogen bond with hydrophilic centers on surfaces within the polymer.

Woo and Piggot [1987a] used results obtained by dielectric methods to argue that water in epoxy forms clusters that are not tightly interacting with the polymer. In a subsequent paper [Woo and Piggot, 1987b] they argued that water accumulated at the interfaces with carbon fibers incorporated in the polymer. This finding may have implications on water interactions with a polymer loaded with mineral particles. Epoxy, however, may be far more adherent to the mineral whiteners of paint than to carbon fibers. Voids where water can accumulate may not exist at interfaces between mineral whiteners and epoxy resin.

Adamson [1980] used a clever combination of thermal expansion measurements and measurements of the swelling of epoxy resins upon exposure to water. He proposed that water first enters the void structure of epoxy resins and then migrates into the polymer network where it hydrogen bonds. As noted by Apicella *et al.*, Adamson also found that epoxy saturated at 368 K would absorb more water when cooled to 274 K. He termed this a “reverse thermal effect”.

Jelinski *et al.* [1985] used quadrupole echo deuterium nuclear magnetic resonance spectroscopy to examine water within epoxy resins. They concluded that there was no free water within the polymer. On the other hand, water in epoxy was impeded in its movement, but was not strongly hydrogen bonded to polar centers. These investigators went further and concluded that water was unlikely to disrupt the hydrogen bonding among polymer segments - a conclusion at odds with that reached by most other investigators.

Zhou and Lucas [1999] examined both water absorption and desorption for a variety of epoxy resins. A desorption curve is shown in Figure 3 for an epoxy made with DGEBA. There is an initial rapid desorption that approaches a constant residual amount of water. This residual water could be removed only by heating the resin to 413 K. Based on these results, Zhou and Lucas argued that two types of water were present in the epoxy - Type I and Type II. The activation energies for the desorption of these types of water were found to be about 42 kJ/mole and 63 kJ/mole, respectively. Zhou and Lucas hypothesized that type I water disrupted the hydrogen bonding among polymer segments and was responsible for the observed swelling of the resin. Type II water, they argued, developed as Type I water evolved within the polymer. They observed that

the amount of Type II water in an epoxy resin increased with both the time and temperature of resin immersion. They speculated that water was evolving from hydrogen bonding with a single hydrophilic center to hydrogen bonding at two centers. They argued that Type II water would reverse some of the swelling and would not plasticize the resin.

The time scale of Figure 3 is noteworthy. Zhou and Lucas used samples that were 0.115 cm thick. Such samples are about 30 times thicker than paint coatings used in the BIP and EPICUR programs. Moisture uptake, if Fickian in nature, should scale with:

$$f(t) = \frac{4}{h} \sqrt{\frac{Dt}{\pi}}$$

where:

$f(t)$ = fraction of saturation water uptake achieved at time t

h = sample thickness

D = diffusion coefficient

Taking the square root of time constant for water desorption observed by Zhou and Lucas to be about 20, the time for paint layers to respond equivalently to a change in the water potential is about 0.8 hours. This time constant for the water content of paint to equilibrate with the humidity of its environment needs to be recognized in experiments with paint.

Zhou and Lucas also reported proton NMR spectra of water in epoxy resin. An example is shown in Figure 4. From the broadening of the resonance in comparison to the spectrum of free water, it appears that water is interacting with the resin in a way that is consistent with hydrogen bonding.

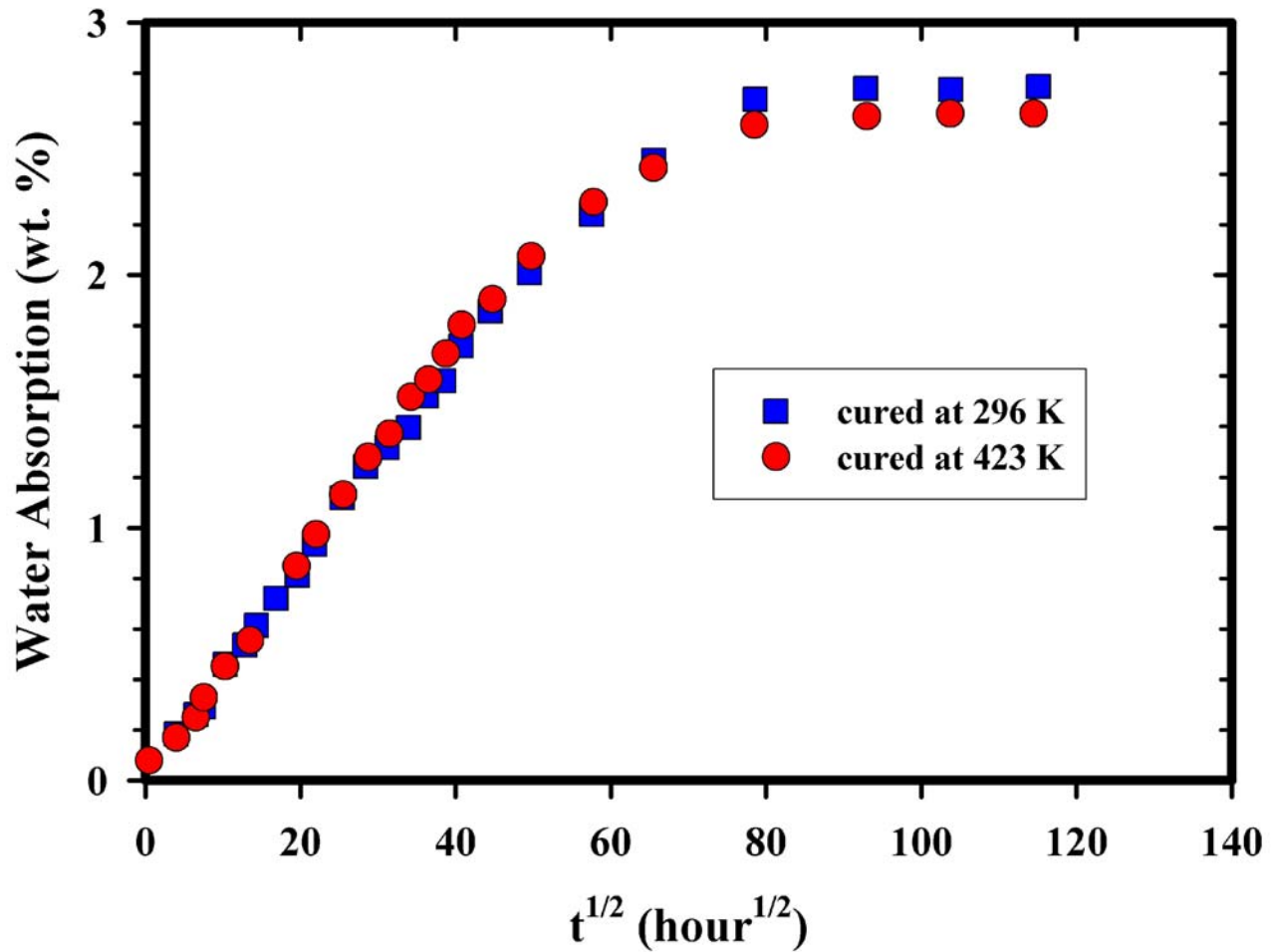


Figure 1. Effects of cure conditions on the water uptake by epoxy resins [Abdelkader and White, 2005].

The PALS method has become very popular in recent years for investigation of epoxy resins [Wang *et al.*, 1990]. The PALS method irradiates a resin with 210 keV positrons emitted from a wafer containing ²²Na attached to the surface. Some fraction of the positrons associate with electrons to form a hydrogen-like species called “positronium”. Two spin isomers of positronium are formed - an ortho form and a para form. The para isomer has a lifetime in vacuum of only 0.125 ns. The ortho isomer has a lifetime, again in vacuum, of 142 ns, so it can be used to probe properties of materials. Decay of positronium in a material occurs by interactions with electrons of the material and produces a 511 keV gamma ray. Decay is more accelerated in the continuum of a

material than when the positronium is trapped in a void. An empirical relationship has been derived between the minimum dimension of a void and the decay time constant of ortho-positronium [Nakanishi and Jean, 1988]. The total intensity of decay events can be related to the volume of voids. By assuming that voids are uniform in size and spherical, it is possible to estimate the void concentration in a solid material [K. Okamoto, *et al.*, 1993]. By making this estimate before and after epoxy resin is exposed to water, some insight into the location of water within voids and the effects of water on the volume of voids can be made.

Soles *et al.* [2000] and Soles and Yee [2000] have concerned themselves with the transport of moisture in epoxy resins. They argue that both the topology of the polymer and the polar centers affect the transport of water in a polymer. To investigate these effects, they fabricated resins with DGEBA and a variety of amines. They created “flexible”, “rigid”, and “extra-rigid” resins. Their “flexible” resins seem to most closely approximate the epoxy resins expected to be in paint. Within the flexible series of resins, they formed resins they termed 40, 60, 80, and 100% flexible. Glass transition temperatures over this series of resins varied smoothly from about 336 to 386 K.

Soles *et al.* define an intrinsic void volume present at absolute zero and a dynamic hole volume the increases with temperature and is produced by molecular motions and thermal vibrations. The “hole volume” available for transport of water molecules into the resin is the sum of the intrinsic and dynamic volumes. These volumes for the flexible series of polymers are shown in Figure 6 as functions of temperature. These “hole volumes are better thought of as narrow channels that are approximated as series of linked spherical volumes. PALS methods were used to infer that the pores have an average diameter of 5-6 angstroms. Diffusion coefficients found for the flexible series of polymers are shown as functions of temperature in Figure 7. The diffusion coefficients of water in the polymers are all remarkably similar. These diffusion coefficients for water in epoxy resin exhibit a dependence on temperature that is similar to that found by Ball *et al.* [2003] for the diffusion coefficient of water in Amercoat 400 epoxy paint although the values for resin are higher than the values for paint.

Soles *et al.* concluded that hole volume affected the initial flux of water into the epoxy resins. Thereafter, there was not a correlation between water uptake and the hole volume. This was interpreted as indicating that water was altering the diffusion pathways in the epoxy resin. Rate limitations on water uptake were found to be associated with the concentration of polar centers in the resin. The limitation on water uptake was attributed to hydrogen bonding of water to polar centers along the very narrow nanopore passages.

Soles *et al.* detected non-Fickian behavior in the uptake of water by the resins. They also found that the total uptake of water reached a maximum and then would decrease (See Figure 8). They suggested that water was removing hydrophilic centers from the epoxy. They speculated that water in epoxy could hydrolyze polymeric linkages formed in the epoxy-amine reaction [Xiao and Shanahan, 1997] [DéNève and Shanahan, 1995].

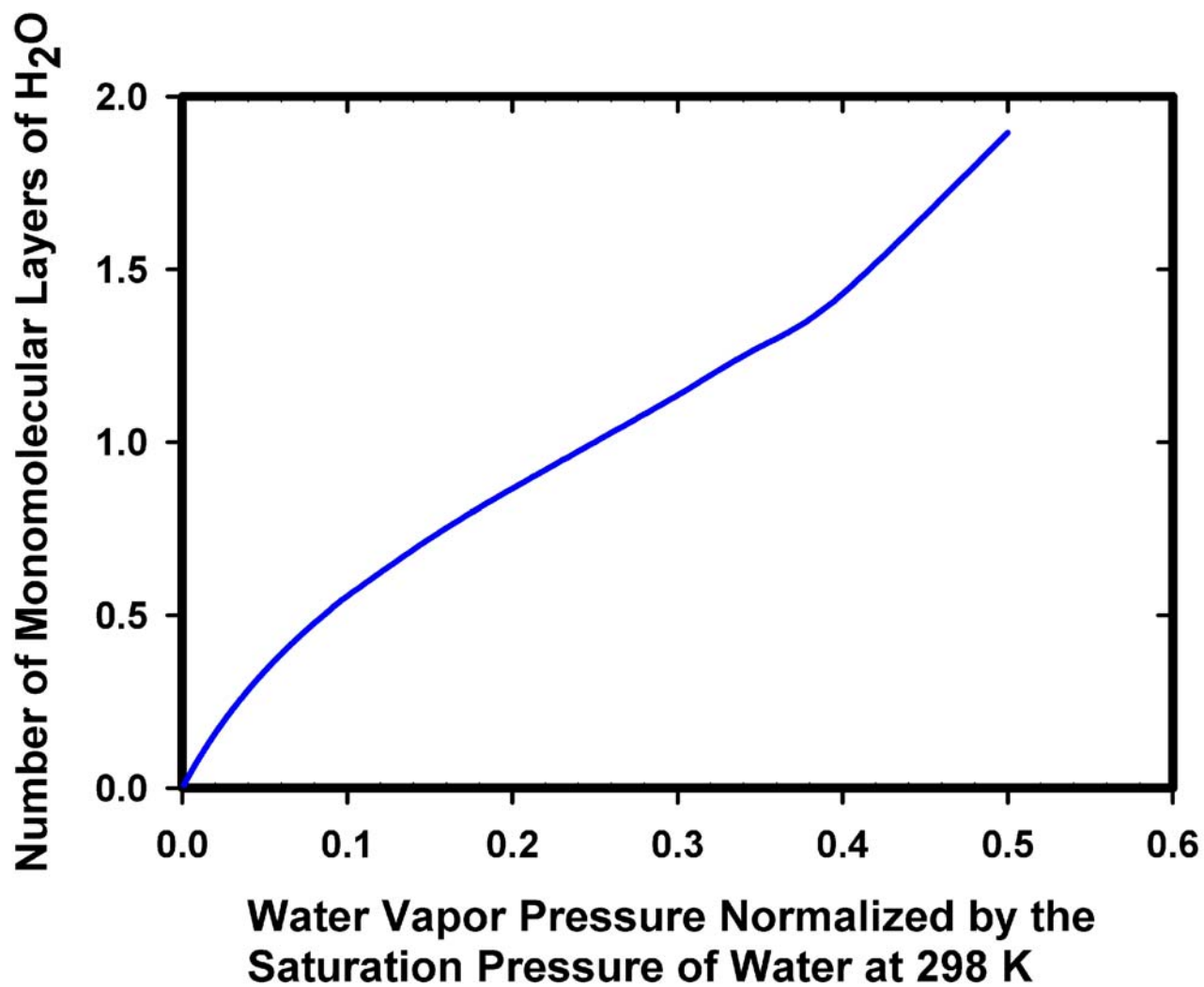


Figure 2. Isotherm for water vapor absorption on epoxy resin at 298 K calculated using BET parameters reported by Moy and Karasz [1980].

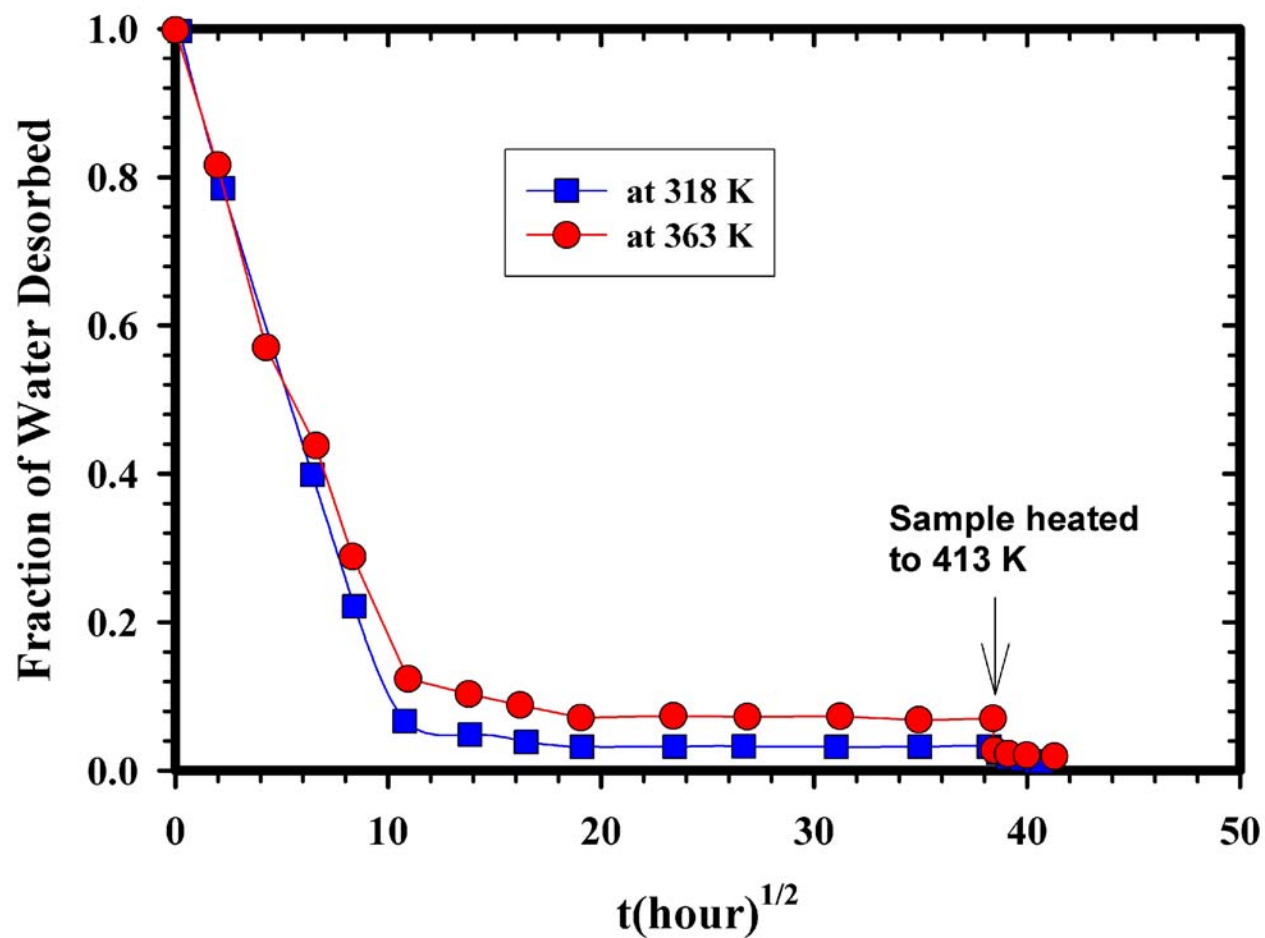


Figure 3. Water desorption from epoxy resins. At about 1450 hours, the epoxy was heated to 413 K to remove the last of the absorbed water [Zhou and Lucas 1999].

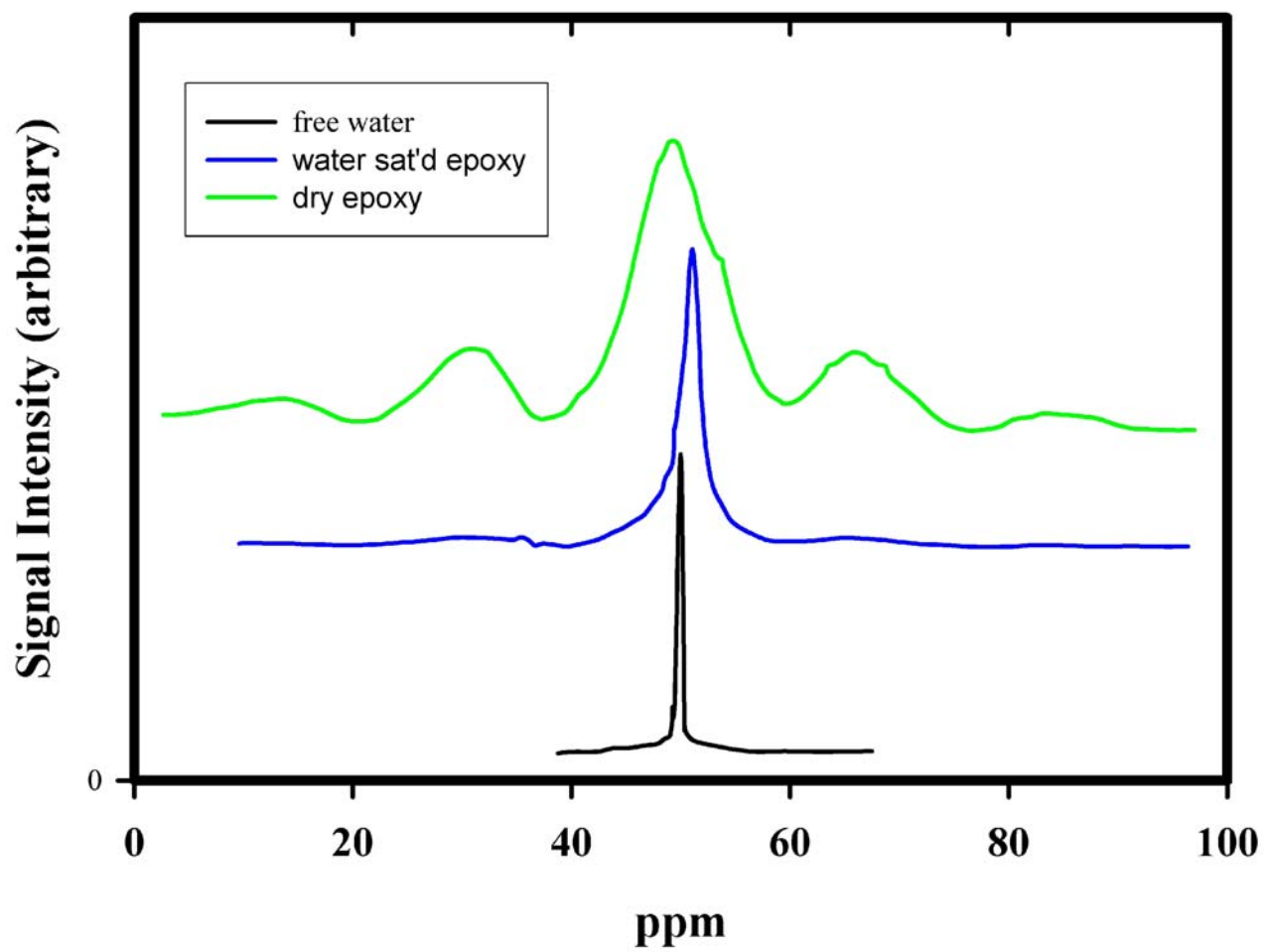


Figure 4. Nuclear magnetic resonance of dry epoxy resin, resin saturated with water and free water [Zhou and Lucas, 1999].

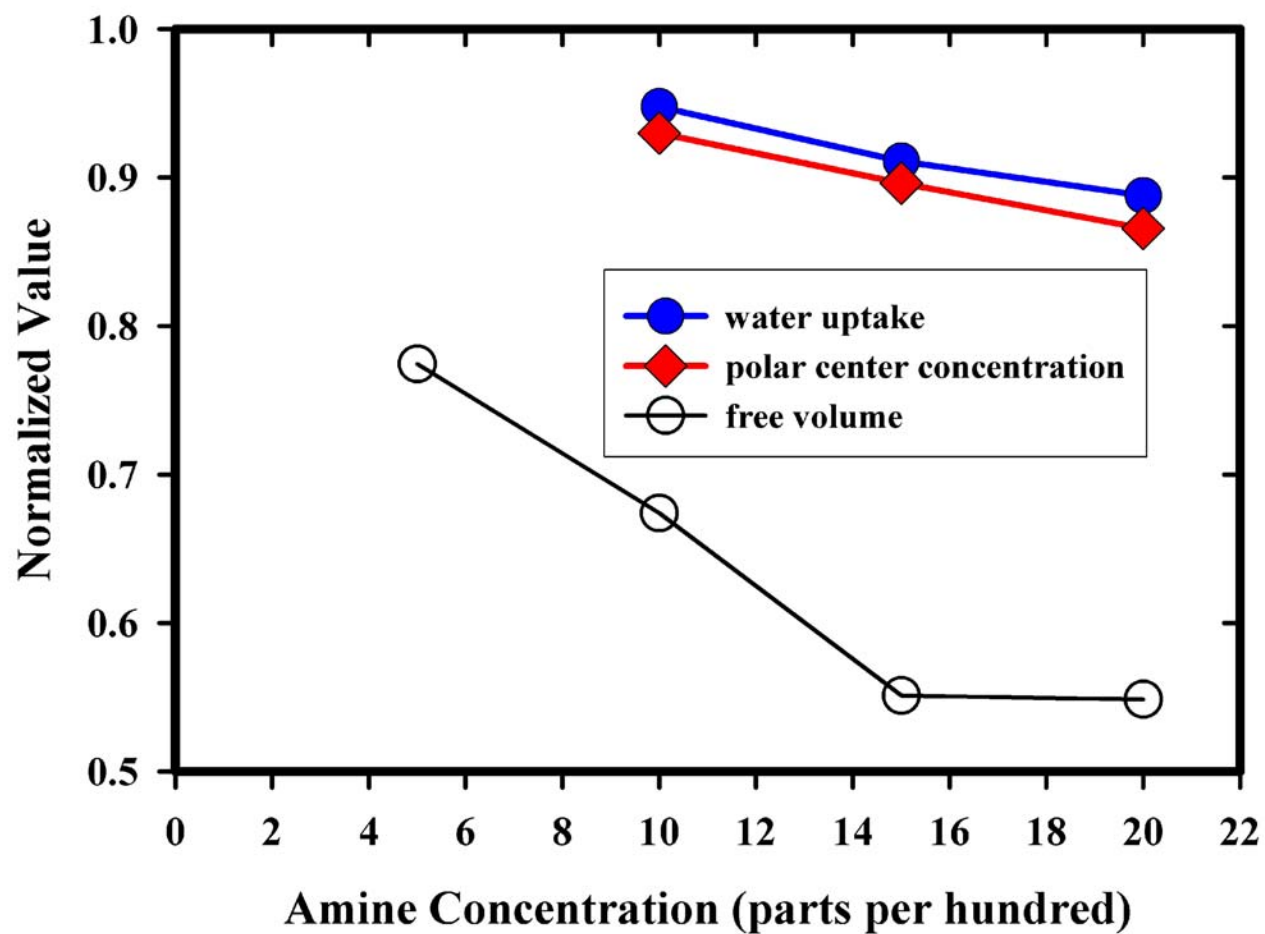


Figure 5. Results showing a correlation of water uptake with polar center concentration rather than void volume [Li *et al.* 2004].

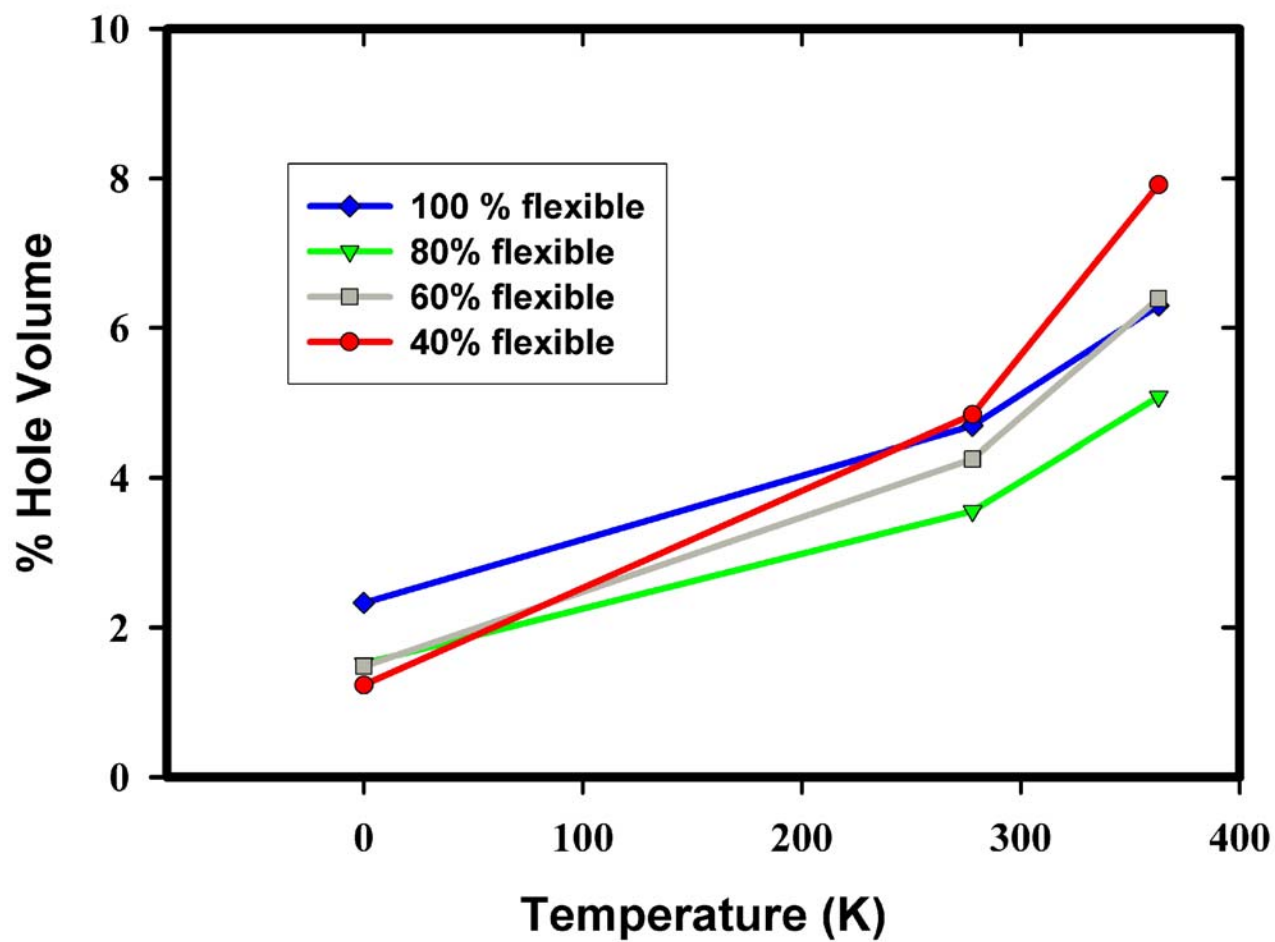


Figure 6. “Hole” volumes found by Soles *et al.* [2000] for various “flexible” epoxy resins.

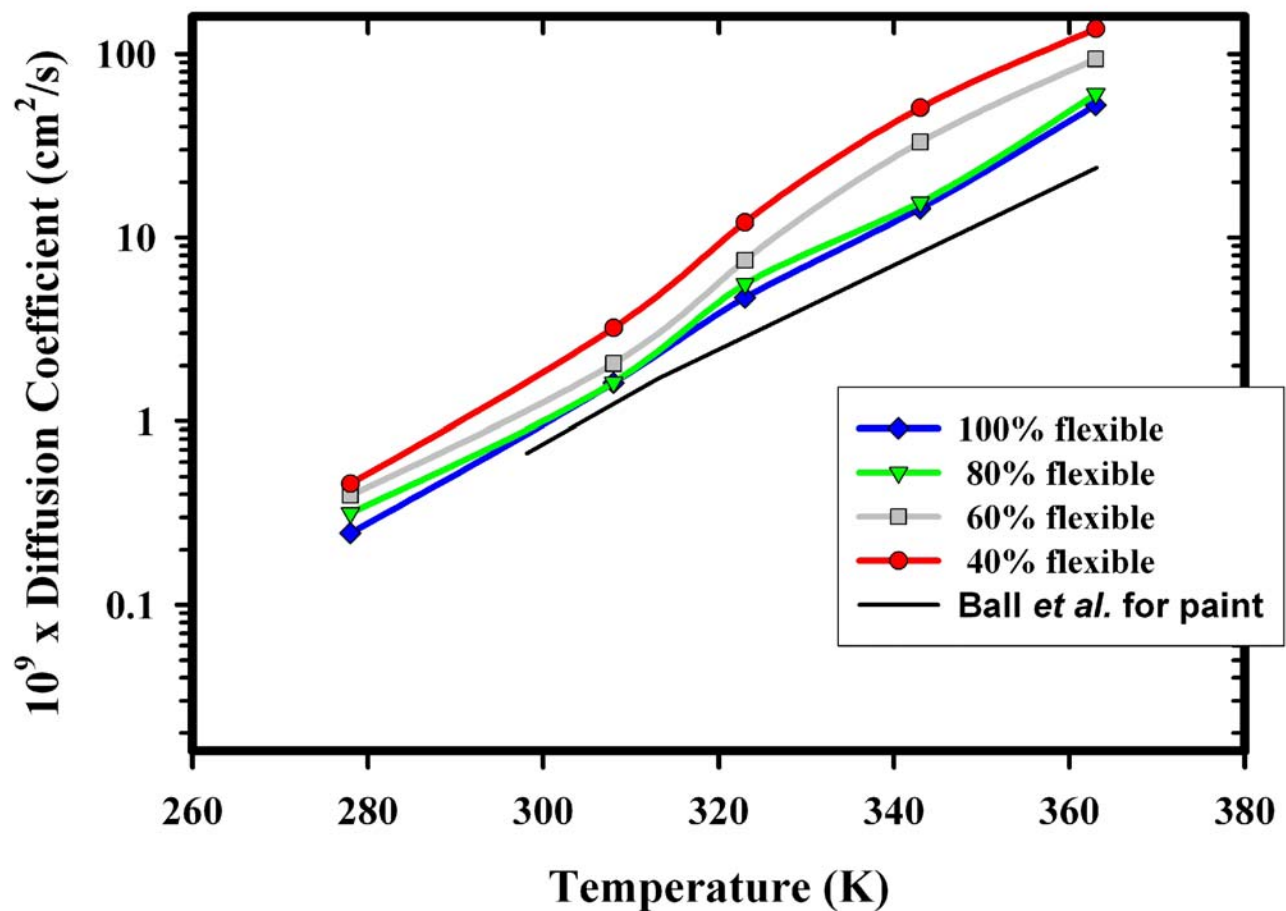


Figure 7. Water diffusion coefficients found by Soles *et al.* [2000] for various “flexible” epoxy resins. The diffusion coefficients found by Ball *et al.* [2003] for water in epoxy paint are shown for comparison.

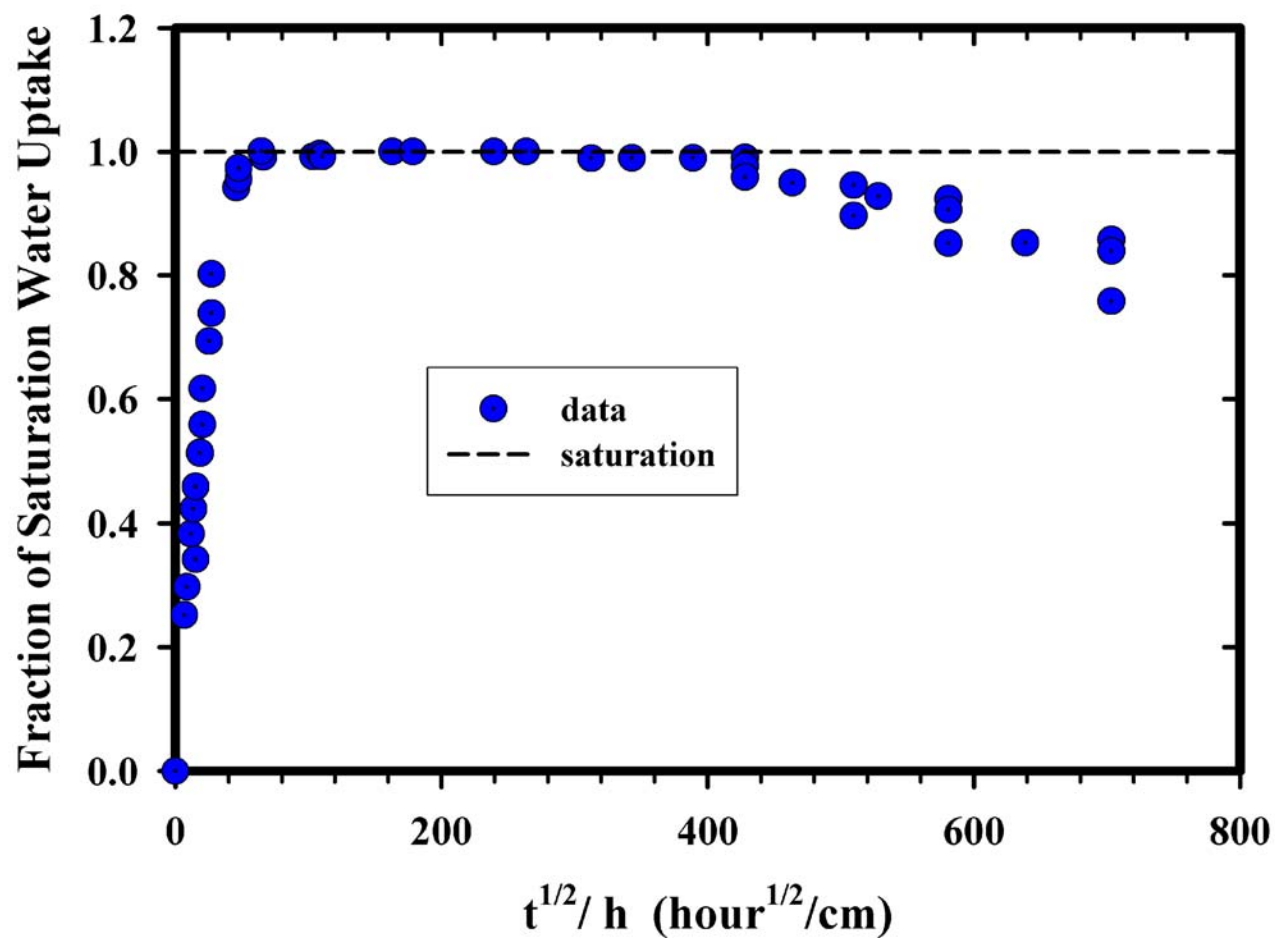


Figure 8. Evidence of polymer degradation by absorbed water [Soles *et al.* 2000]. Note that the time scale has been normalized by the specimen thickness, h .

Soles *et al.* found that damage to the epoxy associated with water absorption affected the diffusion coefficient of water in the epoxy during desorption. They found the diffusion coefficient derived from desorption of water out of the 60% flexible sample to be higher than that during absorption by a factor of 114% at 308 K and 380% at 343 K.

Soles and Lee [2000] suggest that water taken into the epoxy resins is associated with the hydroxy groups on the polymer network. They cite infrared, dielectric and NMR spectroscopy studies to substantiate their suggestion.

IV. DISCUSSION OF WATER ABSORPTION EXPERIMENTS

What emerges from experimental studies is a fairly conventional portrait of water absorption by epoxy resins. Water first interacts with epoxy surfaces that define the void structure of the resin. Water adsorption on the surfaces of the void structure is by interaction with polar centers on the surfaces - probably the hydroxyl groups produced by the epoxy-amine reaction. The interactions with polar species dominates the formation of the first monolayer of water on readily accessible surfaces. The polar interactions of the epoxy surface and water affect less profoundly the development of subsequent monolayers of water. The initial absorption of water is consistent with the BET Type II absorption isotherm. Moy and Karansx [1980] found that deviations developed between the BET isotherm and the experimental observations for partial pressures of water vapor in excess of about half the normal saturation vapor pressure of water.

The BET isotherm is based on the critical assumption that the enthalpy of absorption of all monolayer after the first is equal to the enthalpy of liquefaction of the working vapor. This is clearly not true. The assumption is most radical for the second monolayer. Models that do not make the BET assumption are available and might allow more comprehensive interpretation of water vapor interactions with paint [Thomas and Thomas, 1967].

As the water accumulates onto the surfaces of the accessible void structure of the epoxy, water begins to diffuse into the polymer network. Soles and Lee [2000] interpret this diffusion of water into the polymer network as transport along nanopores that have dimensions not much larger than those of water molecules. The interactions of water along these nano-pores include the disruption of hydrogen bonds among segments of the polymer networks. Polymeric chains will relax and this can create more polymer volume accessible for water. Water diffusion into the polymer matrix comes from more points. The polymer is plasticized and swollen by the disruption of hydrogen bonding and swells.

To this point, the effects of water are reversible in large part. Desorption of water would allow hydrogen bonds to reform. It may take some annealing of the epoxy to recover its stable configuration prior to exposure to water.

As water accumulates in the polymer network, its chemical activity increases. Eventually, the water is able to interact with the polymer in more profound ways than just hydrogen bonding. It can hydrolyze chemical bonds in the epoxy network. The most vulnerable of the bonds is usually considered to be the ether linkages, though it does not appear that this has been proven. Hydrolysis of the chemical bonds in the polymer network will cause damage that is not readily recovered by water desorption. The more permanent damage to the polymer appears to cause some loss of water affinity though the reasons for this are not obvious. What is apparent is that given sufficient exposure to water, there is some water desorption from epoxy resins.

This general scenario for epoxy resins appears quite plausible for the interactions of water with paint. The scenario would need to be amended to account for the many chemical species present in paint that are not present in epoxy resins. Chemical attack on these species could very well delay any attack by water on the epoxy network that results in permanent damage to the network.

An impressive array of experimental methods have been applied to the issues of water absorption by epoxy resins. It is not evident that the results obtained from sophisticated methods such as NMR and FTIR have been particularly elucidating with respect to water interactions with the epoxy resin. In the main, these methods confirm that hydrogen bonding of the water is taking place. The PALS method is proving convenient for the examination of the smallest voids in a polymer network. To date, however, interpretations of PALS results are quite simplistic. Voids are assumed to be uniform dimensional spheres which cannot be correct. It is not clear that the very tiny nanopores

of interest for monolithic epoxy resins will hold the same interest for paints. It is, furthermore, not entirely evident that the PALS method could be so conveniently applied to paints since the void structure may be dominated by interfaces with materials other than epoxy in the paint.

The classical methods of water absorption and desorption still appear to be the most powerful tools for examining the interactions of water with epoxy resins and paints. Absorption measurements have received the most attention. Typically, water exposure is done by immersion. Water uptake is measured gravimetrically for specimens that are 0.1 to 0.5 cm thick. For such thick specimens, saturation requires many hundreds of hours. This allows time for many measurements of the approach to saturation so that reliable estimates of diffusion coefficients can be derived and tendencies for deviations from Fickian behavior can be detected.

Measurements of water absorption using simple gravimetric methods will not be so easy for paint coating that are only 0.002 to 0.01 cm thick. The time required for saturation will not permit characterization of the absorption isotherm so comprehensively. Microbalance methods will be challenging for absorption measurements both because of the usual problems of convection in liquids and because epoxy paint swells as it absorbs water. Other methods need to be considered.

Vapor absorption methods are possible. Water vapor does provide some challenges and with paint it may difficult to rid the material of volatile constituents that will complicate measurements. As noted above there are more advanced models than the BET isotherm to interpret results if adequate methods for measuring absorption isotherms can be found.

Impedence methods for measuring moisture uptake by coatings have been tried often. The capacitance of the coating should be sensitive to the penetration of water since the static dielectric constant of free water is high (~78.3 at 298 K) while the dielectric constant of paint coatings is usually around 4. The usual analysis of impedance methods is based on the equation [Brasher and Kingsbury, 1954]:

$$f = S h(f) \frac{\ln\left(\frac{C(f)}{C(0)}\right)}{\ln \epsilon_w}$$

where:

$C(0)$ = capacitance before water absorption

$C(f)$ = capacitance after absorption of water

$h(f)$ = coating thickness that varies with water absorption

f = volume fraction of water absorbed

S = surface area

ϵ_w = static dielectric constant of water

Hu *et al.* [2003] have used electrochemical impedance spectroscopy (EIS) for epoxy coatings on aluminum. They obtained satisfactory measurement of the diffusion coefficient of water ($2.44 \times 10^{-9} \text{ cm}^2/\text{s}$). They also were able to determine the diffusion coefficient of chloride ion into the epoxy coating to be only $4.67 \times 10^{-12} \text{ cm}^2/\text{s}$. One would not expect iodide ion to have a diffusion coefficient in epoxy any larger than this.

The crucial assumption in the analysis of water absorption by impedance measurements is that the dielectric constant of water is not changed by absorption. This is not true especially when absorption is on polar centers. As a result, the correlation between impedance measurements of water absorption and gravimetric measurements is often not satisfactory. There are occasions when the two methods yield contradictory results [Rouw, 1998]. Improved modeling continues to be explored [Castela and Simões, 2003].

Goossens *et al.* [2003] have developed a very attractive interferometry technique for measuring the change in the thickness of paint films as they absorb water in response to remarkably small changes in the ambient humidity. Over the relative humidity range of 50 to 90%, the thickness of paint has been found to vary linearly with the amount of water absorbed. Of interest is how long it takes for the thickness of paint to reach an equilibrium thickness. An example is shown in figure 9. In this example, the ambient humidity was changed from 60 to 50%. An equilibrium paint thickness was reached in about a half hour. This surely has implication on the conduct of tests of paint absorption involving step changes in ambient conditions.

Goossens *et al.* do remark on the high cost of the apparatus they use for measuring paint thickness. It is also noteworthy that diffusion coefficients they derive from thickness measurements do not correlate especially well with diffusion coefficient derived from gravimetric determination of water absorption.

Desorption measurements have been less extensively used in the study of water absorption. Where they have been used, they have been quite illuminating. Desorption measurements have shown how water absorption changes the water diffusion coefficient in epoxy. They have shown how prolonged exposure to saturated conditions

leads to irreversible damage of epoxy. Desorption measurements have shown that water is bound into the epoxy in energetically different ways.

Desorption measurements can be done using microbalance methods since they do not require the specimen to be immersed in water. Microbalance methods should provide sufficiently accurate and dense data that high quality diffusion coefficients can be derived. Desorption isotherms can be used to infer the nature of void networks and even the geometry of voids in the paint.

Desorption methods have been incompletely exploited. Desorption at various points in the approach to saturation needs to be examined. Desorption after various periods of exposure to saturated conditions or cycling between saturated and unsaturated conditions could be explored.

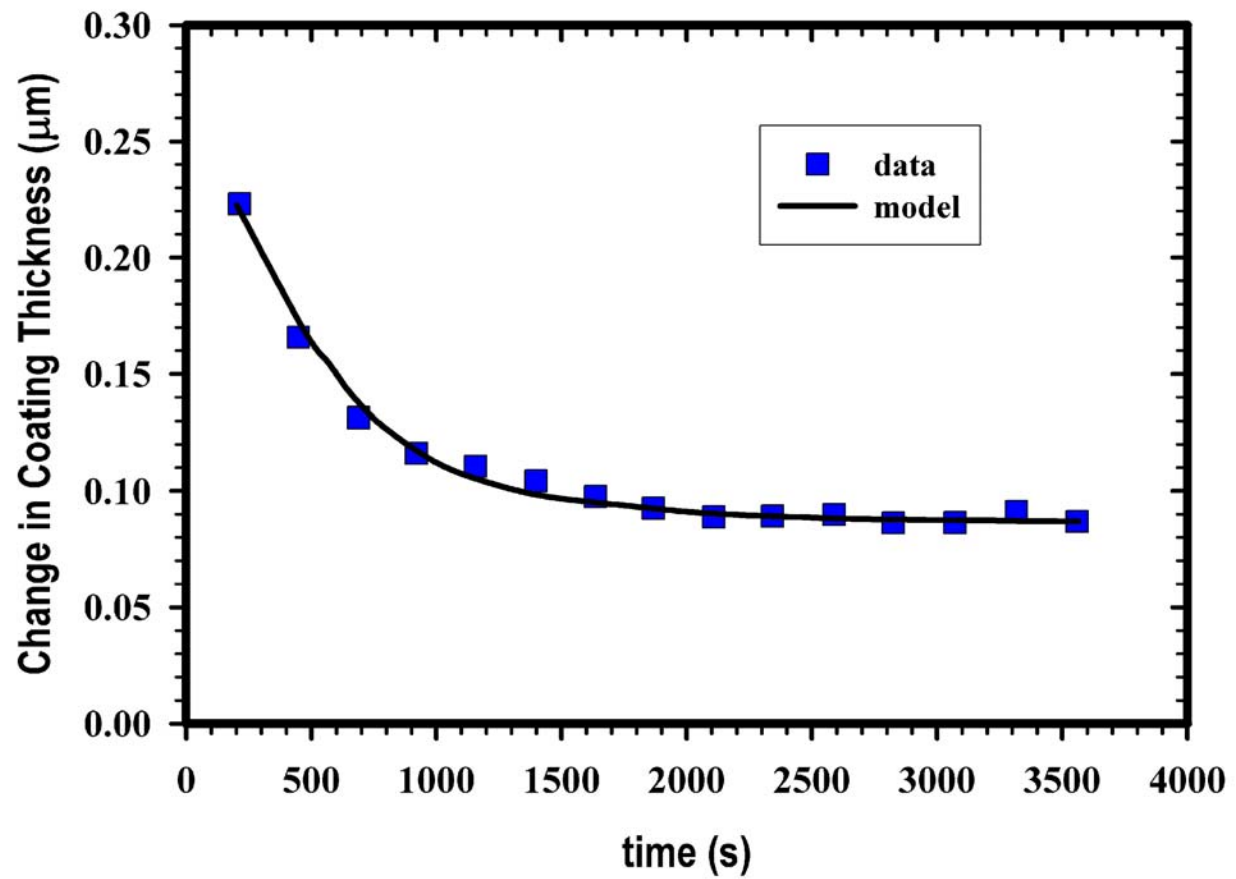


Figure 9. Variation in paint thickness following a step change in the ambient humidity from 60 to 50% [Goossens *et al.*, 2003].

V. CONCLUSIONS

This examination of the chemistry of an epoxy paint and the absorption of water is admittedly incomplete. The examination does allow some conclusions to be drawn:

- Water absorption is endemic to the epoxy resin present in the paint of interest here.
- Water absorbed into epoxy resin associates with polar centers in the polymer. The secondary hydroxyl group of epoxy may be an important water absorption center.
- Water absorption can disrupt the hydrogen bonds among polymer segments and cause the paint to swell. Absorption of water opens the polymeric network and makes more water absorption centers accessible.
- Water absorption may do irreversible damage to the polymer by hydrolyzing linkages such as the ether linkage in epoxy.
- Water desorption experiments appear particularly useful for detecting the effects of water especially any permanent damage to polymers.
- Equilibration of epoxy with water takes time. An allowance for the time it takes paint to equilibrate should be considered in experiments that make sudden changes in ambient humidity.
- The polyamide additive to the epoxy paint may play an important role in the absorption of molecular iodine into the paint. Amides are known to bind iodine perhaps as I_3^- or some other polyiodide. Monitoring changes in the infrared spectra or nmr signals of amide groups exposed to aqueous iodine might help clarify the nature of iodine absorption in epoxy paints.
- The unsaturation of the polyamide additive in the epoxy paint cure should be measured. Residual double bonds in fatty acid chains of the polyamide could be reaction sites for molecular iodine to bind to paint.

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